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**AM'99**

МЕЖДУНАРОДНАЯ  
КОНФЕРЕНЦИЯ  
«ПЕРСПЕКТИВНЫЕ МАТЕРИАЛЫ»  
СИМПОЗИУМ А:  
ИНЖЕНЕРИЯ КОМПОЗИТОВ:  
ИССЛЕДОВАНИЯ, ТЕХНОЛОГИИ,  
ПЕРСПЕКТИВЫ

INTERNATIONAL CONFERENCE  
«ADVANCED MATERIALS»  
SYMPOSIUM A:  
ENGINEERING OF COMPOSITES:  
INVESTIGATIONS,  
TECHNOLOGIES AND  
PERSPECTIVES

# ABSTRACTS

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**MATHEMATICAL AND COMPUTER SIMULATION      1-40**

## MECHANISMS OF ADVENT OF DISSIPATIVE STRUCTURES IN REACTIONARY POWDER SYSTEMS

V.P.Solntsev, V.V.Skorohod

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The matter of making non- equilibrium materials with dynamic stable character (dissipative structures) is widely discussed nowadays considering that possible essential increase of functional properties of materials based on non- equilibrium systems is practically exhausted. Dissipative structures are characterized by higher stability level caused not by bonding strength as in equilibrium objects but the set of interrelated processes leading to collective effect of macrostable system state as a whole. Mechanisms of dynamic stable systems advent are rather evidently ascertained for homogenous chemical systems, where existence of some parallel reactions with feedbacks and autocatalysis effects or substrate inhibiting is the determining factor. There is no doubt the analogous types of chemical interaction occur in topochemical and heterogenous solid systems. A distinguishing feature of these systems and processes is a localized character of chemical interaction at the surface. The next distinctive feature of heterogenous and topochemical reactions is non-isothermal interaction character, caused by the competition of endo- and exothermal effects and heat transfer processes tending to thermo- kinetic oscillations. It makes possible the moving thermal waves generation and following non-uniform development of thermal activated processes, i.e. diffusion, sintering, phase transitions, etc. As a result there appears complex structure differentiating of powder material able to dissipate external energy fluxes which supply energy to non- equilibrium system and its dissipative and regenerating properties.

## THE RHEOLOGICAL MODELS AND DYNAMICS OF MECHANICAL ACTIONS ON MATERIAL BODIES

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Various actions on material bodies are the base of modern technology in material production, testing, and next operation of custom goods. Mechanical actions are dominating among the ones, and in a number of cases other actions reduces to mechanical ones. In this connection deepening the knowledge in the area of mechanical actions on material bodies has as scientific and applied importance.

In the present paper a dynamic analysis is carried out for rheological models of mechanical interaction of machines, having mechanical and hydraulic drives, with elastic, viscoelastic, and viscoelastic strain hardenable bodies in a thermodynamically open system with a single degree of freedom. Just such a system is realised in modern machines for pressure processing and mechanical testing of materials. Dynamic equations are fitting to describe the behaviour of the systems under loading material bodies by a force being less than an elastic limit of the deformable bodies and exceeding the latter. It is ascertained that behaviour of mechanical systems below the body elastic limit is described by the second order dynamic system, that is a system of the first order differential equations in which time is an independent variable. Over the elastic limit of viscoelastic strain hardenable body as well as non-hardenable one loading of the mechanical system follows to the third order dynamic system. The behaviour of a hydraulically loading system is described by the third order dynamic system below the body elastic limit, and the fourth order dynamic system over the body elastic limit. Periodic and aperiodic solutions of the second, third and fourth order non-autonomous dynamic system are obtained taking the transient processes of movement from initial state into account. The transient process of the system movement is ascertained to be either forced damping oscillation or aperiodic damping. The results of calculations for behaviour of mechanical systems at prescribed movement, under the action of constant and variable force as well as at constant loading rate are presented.

The simultaneous action on two series-connected viscoelastic hardenable bodies (or two-layered composite) is described by a system containing two differential equation of the third order and second one respectively, that is by the fifth order dynamic system.

## ANALYSIS AND DESIGN OF THERMALSTRESSED SPACE- REINFORCED COMPOSITE STRUCTURES

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The development of structures used in aerospace, power engineering, in various branches of mechanical engineering is associated with heat resistant materials such as carbon-carbon, carbon-ceramics and ceramics-ceramics composites.

The application of composite thermal mechanics methods play a very important role at a very beginning of the composite development process.

Considering different levels of a composite structure such as fiber - matrix, the representative volume of a composite, a structure made of a composite, it is possible to calculate thermal and mechanical characteristics of a composite at the first stage, and then, these parameters can be used as an initial data for numerical simulation of a structure under the real thermal and mechanical loads.

While designing a composite is considered to be on two structural levels micro- and macro levels. The representative volume of composite is a boundary between these levels.

In a fiber-reinforced composite the following two components can be noted: the reinforcement in the form of continuous fibers and the matrix that fills micro- and macropores of the preform.

The composite matrix is regarded as a homogeneous and isotropic material.

The reinforcing yarn with matrix material being in space between fibers is also regarded as a homogeneous material with transversely isotropic symmetry of its properties.

According to these assumptions the elastic behavior of fiber-reinforced composites is characterized by 7 independent elastic constants of the reinforcement and matrix.

There is some representative composite volume which can be characterized by the mechanical constants as an integral part. These constants depend on 7 characteristics, mentioned above, the component volume content in the composite and on the material reinforcement structure.

Accepting such an approach the thermal and strain-stress state of a composite structure were investigated taking into consideration high level both anisotropy and heterogeneity.

## COMPUTER FORECAST OF THE CAST COMPOSIT MATERIALS

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Generalization of the investigation results of the cast composit materials forming processes made by means of different technological schemes as computer system which is opened developing multilevel structure is presented. Using of this system provide to collect odd information about investigations, properties of the initial materials and cast composit; to prognosis of the processes of making new materials with preliminary determined properties; to obtaine the recommendation on technology improvement; to reduce expenditure on expensive experiments; to provide of storing and searching of conducting investigation information.

The System is based on Data Bank, including results of experimental and numerical research and on knowledge bank, using empirical experience which is the base of the technological processes elaboration for making the cast composit materials. The system is also based on the natural laws of forming materials based on fundamental states of mechanics of continua and dependences obtained as the result of statistical processing of data bank characteristics. It is widely used mathematical models providing simulation of the cast composit materials forming conditions with taking into consideration of their making peculiarity.

System includes some independent part as follows: reference data bank "Properties of Materials" (contents information about composition, physical, thermophysical, machanical properties of materials; extension of data bank is made from reference and science literature); computer system for forecast of properties of composit materials in dependence of material type, mass correlation of components, stress direction ( statistical methods of calculation of macroscopic characteristics of the composites materials are base of the system.Composits materials has chance structure with different degree of order); programming complex for numerical research of the thermophysical peculiarities of the composites materials forming made by different technologies; service programmes for graphic process of the results of computer experiment.

# SIMULATION OF PHYSICS-CHEMICAL PROCESSES AND MACROSTRUCTURE OF METALLIC ALLOYS UNDER SOLIDI- FICATION

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The models and computer software of numerical analysis of heat and chemical processes under ingot cooling and solidification from Fe-based multicomponent melt were developed. Differential equation of Furrie with source, action that is determined of quasi-equilibrium crystallization in models was used [1]. Chemical processes are analysed in unisothermal approximation on basis of fundamental principles of physical chemistry (Gibbs free energy, component activity, interface interaction laws in liquid – crystals – reactions products systems and others). Semiempirical dependencies of dendrites dispersivity from local time of solidification [2]. Account was conducted for the ingot with 0.54 m diameter from Fe-C alloy under overheat liquides on 50°C. One can see, that distances between sec-

r/R	0,9	0,7	0,5	0,3	0
$\lambda_2$ , mm, 0,1%C	0,19	0,34	0,41	0,44	0,45
$\lambda_2$ , mm, 0,1%C	0,56	0,21	0,75	0,76	0,76

ond orders axis's  $\lambda_2$  are depended on alloy composition and coordinate (here it determine local time):

$\lambda_2(r/R)$  go on plateau in accordance with experiment [3]. Owing to these results was determined important parameter - concentration overcooling - growth stimulus of crystals, since temperature deviation from liquidus point in alloys by experimental don't be disclose. Solidification motion in the limits of local time define modification in time of phase composition in the form  $C = C_i S^{k-1}$  ( $C$  и  $C_i$  - current and initial concentration in liquid, respectively; in solid concentration equally  $C_s = kC$ );  $S$  - fraction of liquid phase;  $k$  - distribution coefficient.

Developed method allow to describe temperature and concentration fields under solidification of big volumes, macrostructure and microsegregation of alloys in dependence from heat, physical and chemical initial conditions of problem, which define mechanical and service properties.

1. Borisov V.T. Theory of two-phase area of metallic ingot. - M.: Metallurgy. 1988. - 244p.
2. Flemings M. Processes of solidification. - M.: World. 1977. - 424 p.
3. Golikov N.N., Maslencov S.B. Dendrite segregation in steel and alloys. M.: Metallurgy. 1977. - 224p.



# TO DEFINITION OF FRACTAL MODEL OF CHAOTIC STRUCTURE OF COMPOSITE MATERIALS.

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The fractal model of structure and iterative methods of averaging were used for definition of elastic properties of chaotic structure of composite materials. The critical indexes of volume elastic modulus and Poisson's ratio near the elastic percolation threshold are defined on the basis of numerical calculations.

Investigation of elastic properties for nonhomogeneous medium of random structure with great difference of component properties was carried out mainly by numerical methods on percolation lattices. In particular, the transitions of nonconnecting set of bonds or knots into connecting set and vice versa were investigated. In the critical point  $p_c$  (at the percolation threshold) connecting set was determined to form percolation cluster, which is selfsimilar set, i.e. is the fractal, and volume elastic modulus has scaling dependence.

$$K \approx (p - p_c)^{\tau} \quad (p \geq p_c), \quad \text{in elastic area}$$

$$K \approx (p - p_c)^{\tau} \quad (p \leq p_c), \quad \text{in high elastic area}$$

where  $p$  is concentration of occupied bonds and critical indexes  $\tau, s$  depend only on space dimension  $d$ .

Critical index  $\tau$  which is defined by singular behavior of bulk elastic modulus  $K$  next to critical point  $p_c + 0$  according to data of our calculations is equal  $\tau = 3.25 \pm 0.05$ .

The calculations of highly elastic range ( $p < p_c$ ) showed that critical index "s" depends on elastic properties of phases and changes from  $s = -0.52 \pm 0.02$  at  $K_1 / \mu_1 = K_2 / \mu_2 = 5$  till  $s = -0.75 \pm 0.05$  at  $K_1 / \mu_1 = K_2 / \mu_2 = 0.025$ .

In the neighborhood of the percolation threshold  $p_c$  ratio relationship of bulk elastic modulus to shift modulus  $K / \mu$  ends to constant and results in  $K / \mu = 1.33$ .

At the percolation threshold the Poisson's coefficient is equal to  $\nu = 0.2$ , when  $K_2 / K_1 \rightarrow 0$  and doesn't depend on properties of initial phases for nonhomogeneous medium

PRODUCING COMPOSITE MATERIALS WITH  
PREDETERMINED PROPERTIES ON THE BASIS  
OF BOUNDARY PROBLEM ANALYTICAL SOLUTIONS  
FOR MULTILAYER DESIGNS

V.A.Kudinov, D.K.Nazarenko, R.Zh.Gabdushev, V.A.Oburhov,  
V.V.Nekrylov, S.A.Stefanyuk  
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Studies [1-2] present the results of a new direction of thermal conduction and thermal elasticity boundary problems for multilayer designs. Graphoanalytical method of producing single-layer models for multilayer design specimens has been developed on the basis of the analytical solutions obtained. The method is based on plots of accurate solution for single-layer bodies as to achieve complete agreement between the specimen and model temperatures on the boundaries on the boundaries and at contact point over the entire time span of the unsteady-state process.

To meet this requirement the model is to have time-variable thickness or thermal physical properties. Strict mathematical proof of this assumption based on the law of energy conservation is given in the paper.

The model obtained is used to produce a multilayer specimen with predetermined physical properties and layer dimension. It is possible because the model can fit an infinite number of specimens with varying combinations of layer thickness and thermal and thermal physical coefficients.

Graphoanalytical method of producing a predetermined specimen makes it possible to identify a great number of the required function (temperature, layer thickness, thermal physical coefficients) in various layers of the specimen.

Problems of this kind belong to the category of reverse boundary problems. It is, however, impossible, to solve them with the help of familiar method.

1. Kudinov V.A. et al. Heat exchange and heat inflammation in designs. Samara, Samara state technical university, 1996.-280 pages.
2. Kudinov V.A. et al. Heat mass transfer and thermal elasticity in multilayer designs. Moscow.-Energoatomizdat, 1997.-426 pages.

## COMPUTER MODELING OF PORE SHAPE CHANGING IN P/M DEFORMATION PROCESSES.

V.M. Gorokhov, E.A. Doroshkevich, G.P. Ustinova

In present paper there have been investigated the peculiarities of PM deformation processes on the base of various distributions of structure components within the volume of porous body.

As a result of investigation of plastic zones localization within the porous body under external loading there have been presented the distributions of stresses, strains and densities for powder materials containing pores of different shapes and orientations. It has been shown that plastic zones and stresses concentrations displace near the tops for polygonal pores. The conditions for effective "curing" of pores under external loading have been found. Calculations show that pressures for compaction of metal powders with different pore shapes have their own values in spite of the identity of other properties.

Comparison of the pressures needed for "curing" a pore reveals the substantial decrease in their values when shear strains are used for metal powder densification. Evaluations of stresses, strains and densities for representative elements which model powder materials with the pores of different shapes have been made in the cases of compaction in a rigid die and shear strength test. On the base of these calculations porosity functions in yield equation for metal powders with the pores of different shapes and orientation have been found in the polynomial form. The analysis of obtained results shows the qualitative similarity between the behavior of modeled representative elements with the pores of different shapes and orientation and powder materials under plastic deformation. That is dependence of densification rate on the initial porosity, impossibility of densification up to fully dense state, origination of microcracks near pores at the final stage of compaction.

# METALLURGICAL PECULIARITY OF ARISING OF MICROHETEROGENEOUS IN BULAT STEELS

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These steels have the most unique mechanical and anticorrosional properties and the sound "coloration" during blow also. According to contemporary terminology bulat steels are classified as high- and super-high-carbon steels. The striking expressed chemical and structural micro non-homogenates are the distinct characteristics of these steels. The investigations of this effect carried out by authors [1-3] on the pre-eutectoid steels (0,3...0,6 mass %) demonstrated that it take place after introduction into steel the low-carbon addition at smelt temperature 1580...1620°C. The commination of ferrite layers are observed at two- or three-fold transfer (furnace ↔ ladle). It testify about quazy-eutectoid (colloidal) building of smelt that consist from two areas (L-δ and L-γ obviously). Areas L-δ arised in the result of complete melting of ferrite addition. The investigation of temperature and concentration parameters of existence of delta-areas in hypereutectoid steels showed that introduction of low quantity of addition at temperature 1560...1580°C supply the presence of «inclusions» of structural free ferrite in the solid steel. The time of soaking of melt after introduction of addition make up 8...10 minutes. It was shown that quick solidification of the metal depress the effect of ferrite bandening.

The heterogeneous building of high- and super-high-carbon smelt after introduction and complete melting of low-carbon addition interpret with attracting of domen-dissipative model of liquid. The dissipative structure is observed as additional (new) degree of freedom as long-wave, crystal-vectorially displacements. This dissipative structure fragment crystal during melting on polydomain dynamic system and represent the main artery of mass-transfer and the places of situation of the carbon in steel.

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# COMPUTER MODELLING OF THE NANOSTRUCTURE GROWTH BY THE REACTIVE SYNTHESIS

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Thin films nanostructures have the unique characteristics. The field of their application is various and perspective [1]. The Monte-Karlo method was used for investigation of the nanostructure growth by reactive synthesis [2].

Computer modelling was provided for third dimensional crystal lattices of ZnS, CaF<sub>2</sub> and Mn<sub>2</sub>O<sub>3</sub> -type in <100> direction with interchanging metall and non-metall atoms planes. Film growth was considered as a sequence of stochastic events of atoms adsorbtion, desorbtion or diffusion replacement on the growing crystal surface.

Two possible variants of the growth were considered. For the 1st type the reaction gas atoms were included to the growth surface. For the 2nd type the polarised dipole molecules ( N<sub>2</sub>, O<sub>2</sub> ) were included there. The growth velocity, the surface roughness, the specific density, the vacancies density, the orientation and the form of the crystal germs and another growth parameters were calculated for two model types.

The model results were compared with the experimental data. The growth velocity and the surface roughness didn't depend from the time duration and temperture of the condensation by T <500K for the two model calculations and for the experiment.

The vacancies concentration depedence on the temperature was significantly differing for the two types of the calculation.

For the 1st type the vacancies density was increased by parabolic dependence with the temperature, being practically unchanging for the 2nd calculation type and for the exeperiment.

The far order and diffusion jumps do not influence the growth characteristics at T <500K. If the temperature increases the far order and diffusion jumps may not be neglected in the model.

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## Structure-elasticity model of high porosity sintered materials

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The model of cellular plastic by Gent and Thomas [1] is a system of thin rods random orientation with length  $l_0$  and cross section  $A$ , which connected with polymer balls diameter  $D$ . These balls are considered as not working value of materials, but rods - as working elements of structure. If deformation small the elastic modulus are calculate for formular

$$E_t = E_p \beta^2 / [2(1 + \beta)] \quad (1)$$

where  $\beta = D/l_0$ . Lederman [2] proposed more common equation which lets to considered the influens the begining orientation cellars to elasticity modulus of cellular polymers

$$E_t = E_p (nA/\pi D^2) \beta^2 / [2(1 + \beta)] \quad (2)$$

The member  $(nA/\pi D^2)$  characterese the path of surface of ball which occupy the rods.

The experimental dependences of elasticity modulus four group of high porosity sintered materials on base of copper - powders, fibres, cellars with porosity from 40 to 94% were analised in this work.

The elasticity modulus of investigated materials were discribed by equations (1) and (2), which were worked out for cellular plastic.

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# MATH'S PLANNING AND OPTIMIZATION OF TECHNOLOGY OF GROWING UP PBTE THIN FILMS FROM VAPOR PHASE

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The equations of a regression were obtained by methods of mathematical planning of much factoring experiments. This equations determine relation of thermoelectric parameters of PbTe thin films at the method of a hot wall from technology factors: temperatures of evaporation, walls of the chamber and deposition. Thermo-e.d.f. ( $\alpha$ ), specific electroconductivity ( $\sigma$ ), thermoelectric power ( $\alpha^2\sigma$ ), Q-factor ( $Z=\alpha^2\sigma/\chi$ , where  $\chi$  – is the coefficient of thermoconductivity).

There are some of the regression equations, which are describing the dependence of thermoelectric parameters PbTe films from technological factors:

$$\begin{aligned} \text{At BaF}_2: \alpha, \text{mKB/K} = & -2,459 \cdot 10^4 + 0,186 \cdot 10^2 \cdot T_{\text{II}} + 0,094 \cdot 10^2 \cdot T_{\text{B}} + 0,356 \cdot 10^2 \cdot T_{\text{C}} + \\ & + 2,5 \cdot 10^{-3} \cdot T_{\text{II}} \cdot T_{\text{B}} - 2,2 \cdot 10^{-2} \cdot T_{\text{II}} \cdot T_{\text{C}} + 4,112 \cdot 10^{-3} \cdot T_{\text{B}} \cdot T_{\text{C}} - 9,213 \cdot 10^{-4} \cdot T_{\text{II}}^2 - \\ & - 9,121 \cdot 10^{-3} \cdot T_{\text{B}}^2 - 1,511 \cdot 10^{-2} \cdot T_{\text{C}}^2; \\ Z, \text{K}^{-1} = & -3,409 \cdot 10^{-3} + 0,117 \cdot 10^{-4} \cdot T_{\text{II}} - 0,059 \cdot 10^{-4} \cdot T_{\text{B}} + 0,077 \cdot 10^{-4} \cdot T_{\text{C}} - \\ & - 1,524 \cdot 10^{-9} \cdot T_{\text{II}} \cdot T_{\text{B}} - 1,168 \cdot 10^{-8} \cdot T_{\text{II}} \cdot T_{\text{C}} + 1,085 \cdot 10^{-8} \cdot T_{\text{B}} \cdot T_{\text{C}} - 1,964 \cdot 10^{-10} \cdot T_{\text{II}}^2 - \\ & - 1,977 \cdot 10^{-9} \cdot T_{\text{B}}^2 - 0,565 \cdot 10^{-8} \cdot T_{\text{C}}^2. \end{aligned}$$

$$\begin{aligned} \text{At PM-1: } \alpha, \text{mKB/K} = & 8597,07 - 1,394 \cdot T_{\text{II}} + 9,233 \cdot T_{\text{B}} + 13,544 \cdot T_{\text{C}} + \\ & + 0,012 \cdot T_{\text{II}} \cdot T_{\text{C}} + 0,006 \cdot T_{\text{II}} \cdot T_{\text{C}} - 0,003 \cdot T_{\text{B}} \cdot T_{\text{C}} - 0,014 \cdot T_{\text{II}}^2 - 0,008 \cdot T_{\text{B}}^2 - 0,0083 \cdot T_{\text{C}}^2; \\ Z, \text{K}^{-1} = & -0,515 + 0,872 \cdot 10^{-5} \cdot T_{\text{II}} + 5,393 \cdot 10^{-4} \cdot T_{\text{B}} + 7,647 \cdot 10^{-4} \cdot T_{\text{C}} + \\ & + 0,063 \cdot 10^{-5} \cdot T_{\text{II}} \cdot T_{\text{B}} + 0,033 \cdot 10^{-5} \cdot T_{\text{II}} \cdot T_{\text{C}} - 0,026 \cdot 10^{-5} \cdot T_{\text{B}} \cdot T_{\text{C}} - 0,084 \cdot 10^{-5} \cdot T_{\text{II}}^2 - \\ & - 0,041 \cdot 10^{-5} \cdot T_{\text{B}}^2 - 0,043 \cdot 10^{-5} \cdot T_{\text{C}}^2. \end{aligned}$$

There were determined the ranges of change of technological parameters, for which thermoelectric parameters have optimal values. There was shown that the value of thermoelectric parameters of PbTe polycrystal thin films in several times is bigger then monocrystal PbTe/(111)BaF<sub>2</sub>.

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## Efficient parameters of stochastic magnetic structure in the random field of anisotropy.

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Considered main condition of layered ferromagnetic with the random uniaxial anisotropy. Width of layers is a random quantity. Directions of local axes of anisotropy from layer to layer is fluctuated and arbitrarily distributed.

By minimization functional of free energy received equation system, describing distribution magnetization, from which received expression for the value of magnetization's turn  $\tau$ , showing single-line combination of sinus of double corner of directions EMA of layers. Uniform condition an magnetization considered models not firm, and is divided area into an quasi-uniform magnetization (blocks). For define-thread of efficient parameters of similar structure is considered average of desksides of magnetization  $P(\tau)$ , bringing about the u-turn t.

Way of calculation  $P(\tau)$  closely calls with steepest descent method. Found distribution has of the form of:

$$P(\tau) = \frac{N^N}{N! \sqrt{2\pi\sigma^2}} \exp\left(-\frac{(\tau - \tau_0)^2}{2\sigma^2}\right), \quad (1)$$

( $N$  - a quantity of layers, to which is accumulated magnetization's turn  $\tau$ ).

Apart considered events of regular and casual strife-doing the local axes to anisotropy, but in the same way event of constant width of layer, but random sharing the directions EMA. Shown that parameters  $\tau_0$  and  $\sigma_0$  have an alike type accurate to the numeric multiplier of order units.

Comparison of considered field models to anisotropy allows to draw a conclusion on that that spatial and orientation chaos make a contribution one order in efficient parameters random magnetic structure.

For all three models determined size of area quasi-uniform:  
 $S \approx \delta_0 (a/\delta_0)^{1/2}$ .



## WAVES IN LIQUID-SATURATED POROUS WAVEGUIDES

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Model of porous media can give adequate description of the properties of some real media in various application, including seismology, sound absorption, new materials and other fields. In recent years Biot's theory has been broadly applied to study the waves propagation in fluid-saturated porous media. These theory predicts the existence of two compressional waves and one shear wave in porous materials. These waves have been observed in an experiment (1980) by Plona T.J. For all three waves, the motion of the fluid and solid are coupled.

By now some efforts has been directed toward the study of wave propagation in unbounded fluid-saturated porous media. However, very little progress has been made in the study of wave properties in bounded bodies and waveguides.

The main purpose of this work is investigation of special features of waves propagation in bounded porous waveguides. The wave propagation in fluid-saturated layer whose surfaces are free from stress have been studied. Different variations of free condition on surface of layer depending on liquid behaviour on the surface have been applied. The damping effects were taken into account. In the given work only damping caused by relative motion of different phases (liquid and porous elastic solid) was taken into account. It has been founded that poroelastic material parameters, such as porosity and Poisson's ratio play an important role in the wave behaviour. The structure of normal waves and their dispersion characteristics have been studied. The dispersion depended on the parameters of the porous layer and the type of boundary condition.

The comparison of the wave properties in porous and solid waveguides have been discussed.

## THEORETICAL INVESTIGATION OF LASER OXIDES FILM DEPOSITION

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The models of laser evaporation and film deposition processes were constructed for conditions of real deposition chamber environment. The whole scenario of deposition was divided into 4 stages - heating of target, transport to base layer, condensation of vapor and crystallization of film. The corresponding mathematical problems were solved by means of numerical and simulation methods on personal computer. Programs were written in object programming style with dynamical distribution of memory in Borland Pascal 6.0 language. For laser impulses of 1 ms duration temperature distribution in target corresponds to the Lambert law modified by heat transport phenomena. In vapour phase we obtain velocity distribution law of oxide molecules for target surface temperature conditions. On the base layer surface liquid film condensation gives some definite temperature depending of vapour pressure in chamber. After film deposition abrupt fall of surface temperature gives very high temp of cooling, which depend on initial base layer temperature  $T_0$ , but after some depth under surface we have also region of initial heating. For several  $T_0$  kinetic of crystallisation were simulated on PC with  $100 \times 200 \times 200$  cub. nm film specimen. Two  $T_0$  regions were revealed (from 300 K to 1000-1100 K and above that), in which Arrhenius law have different parameters - one for higher  $T_0$  corresponds to prevaluation of grain grow processes and another - at low  $T_0$  on grain nucleation. Mean grain size values correspond to the experimental ones relatively well.

## COMPUTER MODELING OF PRESSING PROCESS OF SHEET PRODUCTS FROM THERMOPLASTIC FIBER COMPOSITES

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Computer modeling of the sheets pressing process of thermoplastic composites of fiber doubledirectional woven semi-finished products was done. The model involves the heating stage of the semi-product and the process of its compression and monolithisation.

The model of the heating of fiber semi-products is based on the parabolic differential equation of thermal conductivity connected the heating parameters - the time and the temperature with the point coordinates in the heat spreading direction. Based on the analysis of the regular unstationary heat spreading process in the semi-product the functioning formula of the semi-product heating parameters depends on the structure of woven semi-products, the number of layers and the chemical composition of the material components was received, so we can find the heating time of the semi-product to the needed temperature. The computation of the effective heat conductivity of fiber semi-finished products is based on the structural scheme of the system of heat resistances repeated the semi-finished product structure.

The model of the pressing process is considered as a double-staged process with the stages of «dry» compression and the following impregnation process taking into consideration the pressure losses after the deformation of elastic reinforced fibers. The impregnation process of reinforced fibers is described in the base of the Darsier law taking into consideration the disposition of the melt-coating process because of the resistance of pinched between fibers air. Analytical formulas to count the impregnation time and the residual porosity of the product depending on the temperature of the semi-product and the pressure was received, and also the formula to count the permeability coefficient reinforced fibers.

The models are adequate with the results of the experimental researches of the process. The results of the researches are realized as a complex computing program. This program is the base of construction of the automate designing system of technological process of producing products from the polymer composite materials.

# COMPUTER MODELLING OF THE PHOTOSTRUCTURAL CHANGES IN $As_2(S, Se)_3Sn_{0.1}$ ALLOYS.

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In this report we advise that the study of the composition of condensed molecules by means of mass spectrometry and HyperChem Computational Chemistry Program may harvest complementary information about structural models of chalcogenide glasses and mechanism of the photostructural changes.

Data of mass spectrometric analysis of  $As_2(S, Se)_3$  glasses prepared by special techniques shows the perceptible difference in the value of the ion currents corresponding to the  $As_m(S, Se)_n$  molecular units before and after illumination, detected at low vaporisation temperature (393 K for  $As_2S_3$  & 433 K for  $As_2Se_3$ ) and low ionising electron energy (20 eV). Our data of the computational calculation of the stableness of suchlike molecular units are also in correlation with mass spectrometry data. After laser illumination we detected some new kind of molecular units as  $As_m, S_n$  and  $Se_n$ . The observed changes in the mass spectra under illumination may be explained in view of some re-arrangement of the component atoms in the shot-range order.

In this communication we submit also the results of computational modelling of molecular units as  $As_m(S, Se)_n$  detected by mass spectrometry in the  $As_2(S, Se)_3Sn_{0.1}$  alloys before and after laser illumination. Using HyperChem Computational Chemistry program we realised 3D structures, with minimum energy conformation [kcal/mol], for the following molecules:  $As_4$  [3.47];  $S_8$  [4.44];  $As_4(S, Se)_3$  [11.87 & 80.26];  $As_2(S, Se)_5$  [14.36 & 148.03];  $As_2(S, Se)_4$  [17.62 & 115.42];  $As_2(S, Se)_6$  [19.11 &  $As_2(S, Se)_3$  [25.81 & 97.18];  $As_4(S, Se)_6$  [43.13 & 184.33].

At the same time we proposed the models of the  $As_2(S, Se)_3Sn_{0.1}$  alloys by using for computational modelling 200 As atoms, 300 (S, Se) atoms and 10 tin atoms. Suchlike models shows that the tin atoms may be bonded in two ways: in the event of that the tin atoms are mutual for two rings with 12 atoms and the case when the tin atoms are bonded among the layer of the glassy network. The structural model shows the increasing of the density of packing of the atoms when the tin atoms are inserts in the netting rings for 12 atoms.

# COMPUTER SIMULATION OF 3-DIMENSIONAL NETS DEFORMATION

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The 3-Dimensional net deformation model were developped for spherical and equidistant termo-mechanical treatment of cloathings details by pressure equipment. The mathematical model includes Chebyshev approach in 3-Dimendional nets treating and Southwell relaxation technic for solution of obtained problem. Corresponding algorhytms and software were developped in object programming frames by use of Borland Pascal Compiler on Pentium PC. Net model contained 400 nodes of square-cells, which may change as well cells chains as cells angles letting the Net to be adjusted to the press surface. The local deformation was managed by such parameters as press surfaces radii and trybomechanical properties of treated details. Simulation results are well correspond to the experimental data. Obtained Model may be explored also in other net's deformation situations.

# LAWS OF CAPILLARY TRANSPORT OF A SOLVENT OF IMPURITY WITH ZONE MELTING OF POWDER MATERIALS

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It is shown by methods quantitative metallography, that with zone melting of green bodies with porosity 35-45 % from powders borides REM,  $TiB_2$ ,  $ZrB_2$ ,  $HfB_2$ ,  $B_4C$  and their eutectic mixes of structure with the additive, as a solvent of impurity (I), 2 vol.% of a boron, the structure of green body is formed in a field of a large temperature gradient (1300 K / sm) and represents a skeleton of particles of a refractory material (RM) penetrated connected pore channels which cross size, as well as the size of particles RM, is increased, and their amount decreases in process of increase of green body temperature.

Pore channels are filled by liquid (I) partially, which is gone under action of capillary forces in a field of a temperature gradient.

The change of the particles size RM in process of a recrystallization through driven liquid I is satisfactorily described by the equation of a diffusion coalescence with the account of a convective part of mass transport RM through liquid I.

It is offered the computer model of capillary transport I, which includes: - the physical model of a structure of a powder initial preparation, according to which the preparation is represented of many layers green consisted of spherical particles RM, which identical size within the limits of one layer and this size is continuously is increased from a layer to a layer in the process of a temperature increase;- the mathematical description of a processes of a growth of a grain RM and capillary mass transport of a liquid I in account of friction forces of liquid in a surface of pore channels; - the computing algorithm allowing to determine the size of a grain, capillary mass pressure, temperature, the speed of a liquid movement and parameters consecutive in thin layers with constant temperature.

With the help of the computer model the influence of physics and chemical properties of powders RM and liquid I, thermal and temperature-temporary conditions zone melting, dynamics of change of the geometrical characteristics the green body structure on the speed of moving of a solvent on porous preparation in a field of a temperature gradient is investigated. It is shown that with speeds of melting zone movement  $< 1$  mm / min. Liquid I has time to leave from porous channels of initial preparations of the given structures and does not get in front of melting of RM, that enables effectively to apply for zone melting porous powder preparations and growth crystals of high chemical and structural perfection.

# THE ELECTRICAL CONDUCTIVITY OF THE FIBROUS POROUS BODY WITH UNPERFECT INTERPARTICLE CONTACTS

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The dependence of electrical conductivity of the porous material from the discrete fibres with chaotic orientation was determined analitically.

With the use of the theory by R.Holm [1], the quantitative relation between the electrical resistance of a single contact  $R$  and its relative size was established. In the case of a short onstriction that is observed in the sintered fibrous materials (that is when the size of contact becomes compatible with the diameter of a fibre  $d$ ) the following expression was devived:

$$R = \frac{2\rho_0}{\pi d} \left[ \frac{1}{\xi} \operatorname{arctg} \frac{\sqrt{1-\xi^2}}{\xi} - 1,2\sqrt{1-\xi^2} \right], \quad (1)$$

where  $\rho_0$  - electrical resistance of the substance of fibres. Considering the single fibrous particle of length  $L$  with the regularly distributed circular interparticle contacts of diameter  $d$ , the following expression of electrical conductivity of model fibrous body was obtained:

$$\lambda/\lambda_0 = \left[ 1 - \frac{A}{2L/d} \ln \left( \frac{2L/d}{A} + 1 \right) \right] \lambda_0/\lambda_0, \quad (2)$$

where  $A = \frac{1}{\xi} \operatorname{arctg} \frac{\sqrt{1-\xi^2}}{\xi} - 1,2\sqrt{1-\xi^2}$ ,

and  $\lambda/\lambda_0$  - relative electrical conductivity of fibrous material;

$\lambda_0/\lambda_0$  - relative electrical conductivity of fibrous material with perfect interparticl contacts versus porosity by the V.V.Skorokhod model [2]. The calculated values of the size of interparticle contacts are close to the data from literary. The linear of dependence  $\xi^5 = f(t)$ , obtained with the use of experimental data on electrical conductivity at isothermal endure of material also confirm the validity of the obtained expression.

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## THE DATE BASE FOR THE CONSTRUCTION HETEROPHASE MATERIALS

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Using of system of mathematics modeling oriented on problem under examination as well the date base for physics and mechanics material properties rises the effectiveness of material research.

The date base system "The maps of physics and mechanics properties of the construction heterophase materials" is developed in Institute for Materials Science. System subject field of developing production and using of new materials is presented as a multimesured space of the material properties and characteristics as well the function criteria and production technology.

The information and program tools of system allow to decompose of the subject field and to present of decomposition results as diagrams similar to Eshby ones in accordance with the problems under examination. Using logarithmic scale allows to show the properties of materials that can differ by several orders. The data for each material class are represented as the closed fields.

Unlike another date bases and automatic systems of research in the fields of materials properties and mechanics of materials this way for constructing material properties map allows to estimate the production technology effect on properties of material and to optimize the technology conditions.

By means of appropriate choice of axes and scales of material property maps the additional characteristics may be received for extensive class of structural elements. This characteristics are defined with combining of various material properties. The map may be used for testing date and existence of developing material novelty. They may be used for the choice of materials for various construction elements at the early stases of design.



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## SOLUBILITY RESEARCH FOR BINARY AND TERNARY METAL ALLOYS

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Ccoupled thermodynamical-mathematical approach was developped for metal alloys solubility description in binary and ternary systems. It includes as well as statistical models of solid and liquid solutions and phenomenological models for tie-lines evaluation in all possible phase equilibria cases. All obtained data are based on international SGTE Standard Values for Entalpy and Entropy temperature-pressure dependences and widely known CALPHAD optimization procedures. The new version of coupled assessment for Ti-Mo, Ti-Sc, Ti-Al, Sc-Al systems gives demonstration of developped technic. For the ternary Ti-Sc-Al system it gives resonable prediction of possible phase equilibria diagram, for which we have only few experimental data.

### MODELING OF GROWTH OF A DIAMOND-LIKE FILM ON A SURFACE SIC.

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Silicon carbide may be used as a substrate for growing synthetic diamonds and other less-common modifications of carbon. Formation of carbon films and/or clusters is a critical stage of any such process and understanding of their properties is essential for development of new technologies. Moreover, particles of silicon carbide themselves may be formed in other technological processes, and play a role of nucleation centers for diamond growth.

In this work the method of molecular dynamics (with the use of Tersoff's empirical interatomic potentials) was employed to investigate the process of growth of diamond-like film on silicon carbide surfaces with various crystallgraphical orientation at high temperatures (1000–2000K). The geometrical characteristics of carbon films and stability of their structure were investigated. The structure and stability of carbon clusters of various forms on the silicon carbide surface were also studied for temperatures within the above-mentioned temperatures interval.

THE INVESTIGATION OF MAXIMUM HYDROGEN  
SATURATION LEVEL OF HYDRIDES OF TRANSITIONAL  
METALS WITH CUBIC STRUCTURE

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Hydrides of metals with cubic structure are investigated using non-local pseudopotential. In contrast to generally adopted approach in this work most probable geometric location (position) of hydrogen atoms in crystal lattice is not fixed. It is assumed that metal atoms form face-centered cubic lattice, and hydrogen atoms are located between lattice sites in any place, their number per one atom of metal varies from one to maximum number.

The problem consists in the following:

to find maximum number of hydrogen atoms dissolved in hydride of transitional metals and determine the stable state.

To achieve this purpose full energy of hydride as a function of the number of hydrogen atoms is calculated. Comparing full energy for various compounds most stable state is obtained.

It is proposed to construct the pseudopotential in the following way:

$$Y = Y_M \frac{\Omega_M}{\Omega} + x Y_H \frac{\Omega_H}{\Omega},$$

where  $Y_M$  and  $Y_H$  - pseudopotentials of metal and hydrogen,  $\Omega_M$ ,  $\Omega_H$  - atomic volumes,  $x$  - number of hydrogen atoms,  $\Omega$  - volume of compound.

With the help of perturbation theory full energy of the system is calculated by the second order of pseudopotential.

Full energy of the system is a function of the number of hydrogen atoms. Investigating the function extremum the value of  $x$  when the energy is minimal and the state is stable can be found.

Lattice parameter and volume compressibility module is calculated for investigated systems.

**Structure-deformation model of high porosity sintered materials**  
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The structure model of high porosity materials (HPM), consisting from dodecahedrons, which consisted from rods are considered. The main element of material structure was the sistem from four rods which are situated as a tetrahedron. To make axial load, can receive deformation these structure elements as a sum of axial and bending deformation. Common deformation structure elements is

$$\varepsilon = \varepsilon_p (1 + \sin \psi + l^2 \cos^2 \psi / (7d^2) (1 + \sin \psi)) \quad (1)$$

where  $\psi$  - the angel between the incline rod and its projection to plane which normal to load,  $l$  and  $d$  - length and diameter of rod,  $\varepsilon_p$  - uniform deformation (tensile or compression) of rod from matrix material. If  $\psi = 0^\circ$  - the elastic deformation HPM must be maximum, but if  $\psi = 90^\circ$  - minimum and is equal  $\varepsilon_p$ , the analysis of model (1) was shown. The comparison of calculated and experimental results  $\varepsilon_{-1}$  - limit cycle deformation fibers HPM [2] was show, that if porosity is not great (43%) the calculated results of deformation are more then experimental in 1.45, but if porosity great (77%) - in 1.07.

**Literature**

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COMPUTER SIMULATION of DEFORMATION and FRACTURE  
PROCESSES in LAMINATED COMPOSITE MATERIALS  
of SYSTEM Cr-V

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With the help of further development of a mathematical method [1,2], permitting to simulate of deformation and fracture processes of laminated composite materials, the improved version of computer model is developed and are calculated from it by the help strength and plasticity characteristics of laminated materials of a system Cr-V in a broad interval of thicknesses at room temperature. The reliability of model is confirmed by high coincidence computational and experimental data.

The model takes into account statistical distribution of defects and heterogeneities of a material, influence of irregular deformation to process of fracture, and also influence intermediate phases on mechanical properties of a composite material.

The model is applicable for prediction strength and plasticity properties of composite materials of a diverse structure at various temperatures and hereinafter will become the basis for development of models permitting to calculate impact viscosity of composite materials and to investigate influence to their properties radiation irradiation.

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# GRADIENT OF FILTRATIONAL PARAMETERS IN THIN POROUS MATERIALS

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Gradient of filtrational parameters in thin layers of porous powder materials was determined using as example twisting factor of permeable materials.

It was shown that for the model of a porous material having intersecting capillares of similar lengthes  $\Delta L$  and different radiuses  $r$  in the form of cubic lattice local twisting factor of way  $\xi_i$  for gas grows with distance from the boundary surface. Values  $\xi_i$  grow with reduction fractional of conductional bond  $a$ . And, than less this share ( at and more critical ), theme more the distance from boundary surface at which it becomes stable.

The maximal local twisting factor for gas at threshold share of conductive bondes  $\xi_i$  is 56.5. It is reached at 34 layers.

The average twisting factor  $\xi$  of porous material of a thickness less or some the greater 34 layers is defined on formula

$$\xi = 1/n \sum_{i=1}^n \xi_i.$$

The casual nature of porous structure renders to opposite case of local factor twisting the influence on the critical pore size of material ( also in area of small thickness). It also causes gradientional of its behaviour.

The thickness of material also provides enough the considerable influence upon the permeability and por average size without availability of capillar effects when the material thickness are small.

ENERGY BAND STRUCTURE, CHEMICAL BONDING AND X-RAY  
SPECTRA IN  $\text{TiH}_n$  ( $n=1,2,3$ ).

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Equilibrium lattice constants for existing ( $\text{TiH}_2$ ) and hypothetical ( $\text{TiH}_{\text{octa}}$ ,  $\text{TiH}_{\text{tetra}}$ ,  $\text{TiH}_3$ ) compounds were calculated within the full-potential linearized augmented plane waves method (FLAPW). Electronic band structure, total and partial density of states were determined for each of these lattice constants. Comparison analysis of chemical bonding was performed.  $K$  and  $L$  X-ray emission spectra and  $K$ -absorption spectrum of titanium were calculated in dipole approximation in all hydrides. The results are compared with each other and with available experimental data.

AB INITIO CALCULATIONS OF RAMAN FREQUENCIES IN  
DEFORMED DIAMOND CRYSTAL.

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The full-potential linearized plane-waves method (FLAPW) was employed for calculations of the full energy of diamond crystals as a function of lattice parameter and the degrees of deformation. Frequencies of  $\Gamma$ -phonons were calculated by numerical differentiation at different deformations. Conclusions about the possibility to use Raman spectroscopy for experimental estimation of degree of local deformations in diamond are done.



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PHASE EQUILIBRIA CALCULATIONS FOR Ti-H AND Zr-H  
SYSTEMS.

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IPM NASU, Kyiv, Ukraine

Total energies as functions of lattice constants for  $\text{MeH}_2$ ,  $\text{MeH}_3$ ,  $\text{MeH}_{\text{oct}}$ ,  $\text{MeH}_{\text{tet}}$  ( $\text{Me}=\text{Ti}, \text{Zr}$ ) were calculated within the full-potential linearized augmented plane wave method (FLAPW). From these dependences equilibrium lattice constants and appropriate total energies were determined. Based on these data the Ising-type model for phase equilibria calculations in Ti-H and Zr-H systems was formulated and its parameters were determined. With the use of mean field approximation of statistical theory of alloys the phase diagrams metal-hydrogen were evaluated and chemical potentials of hydrogen vs temperature and concentration were obtained. Conclusions about the conditions at which formation of metastable titanium and zirconium three-hydrides phases is possible are done.

# **NORMALIZED MECHANICAL CHARACTERISTICS OF HIPOROUS MATERIALS AND SANDWICH STRUCTURES WITH POROUS CORE UNDER BENDING**

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A method of comparative analysis of mechanical behaviour of compact and powder beams under bending is described. The technique to determine different normalized parameters characterizing relative properties of compact and powder beams is proposed. For high porous materials with pore-former powder the influence of porous space structure characterized by parameters  $m$  (the ratio of the pore forming material and powder particle sizes) and  $\theta$  (the volume fraction of pores) on mechanical characteristics is shown.

A comparative analysis of specific mechanical characteristics for sandwich type porous laminated composite under bending is made. External layers of such composite are compact while internal layer consists of highporous material obtained by using of powder former. The dependences of specific stiffness, strength and yield load on the volume fraction of pores  $\theta$  and porous to compact layer thickness ratio  $m$  are considered. Variations of  $m$  and  $\theta$  is shown to affect the gain in stiffness, strength and yield load when weight of the composite is constant.

In the case of the equal sizes of compact and porous beams relative stiffness  $k_k$  is always less than the unit but in the case of the equal weight biporous materials demonstrate essential weight advantage. The relative stiffness maximum ( $k_{km} = 6$ ) is observed in the optimal structural state (for biporous nickel whose structural parameters are  $\theta = 70\%$  and  $m = 50$ ). It means that under equal loads such a porous beam has deflection one-sixth as large as that of the compact beam which has the same weight; i.e., under condition of equal deflection the porous beam has load six times as much as that of the compact beam, the effect for other biporous materials is lesser. Biporous materials demonstrate the gain in weight at the same stiffness. Under optimal conditions this advantage is 1.85 as much as for the compact materials.

Biporous materials also demonstrate the essential gain in yield load for the same weight and weight advantage at the same yield load but this advantage is less as compared to that for elastic deformation. It is important that powder materials without pore former do not give an advantage.

Maximum gain in stiffness and yield load of layered beam compared with that of the compact beam of the same weight for unchanged porosity and the structure of porous space is achieved when a definite ratio of porous to compact layer height is obeyed. For biporous internal layer with porosity 75% the optimum relation of these heights for stiffness is  $m=20$ , in this case gain in stiffness is 9.6. The optimum ratio of heights  $m$  for yield load for porosity 75% is 10. Maximum gain in yield load in these conditions is 3.3.

Maximum gain in the weight of layered beam compared with that of compact beam having either the same stiffness or the same yield load for unchanged porosity and porous space structure is also achieved when the definite ratio of porous to compact layer height is obeyed. For biporous internal layer with porosity 75% the optimum ratio of heights for the same stiffness is  $m=20$ . In this case gain in weight is 2.1. The optimum ratio of heights  $m$  for the same yield load for porosity 75% is 10. Maximum gain in weight in this case is 1.8.

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## VISCOSYELASTIC PROPERTIES OF FRACTAL SYSTEMS

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High Mathematics Dept

It was considered time dependencies of fractal sets for analyzing of viscose and elastic properties of unordinary systems. It was constructed fractional derivative, which is connected with fractal indexes. It was obtained the connection between relocation and fractional derivative. This gave a possible for explanation of experimental data of unordinary systems.

## CRITICAL BEHAVIOR OF DIELECTRIC PROPERTIES OF TWO PHASE COMPOSITES

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We have considered two problems of dielectric properties of metal-insulator composites. We have described a dielectric breakdown scaling relation using the renormalization group approach. Application of the real space renormalization group transformation technique to the problem of dielectric behavior of percolating systems permitted estimation of the corresponding critical indices. Secondly, we have evaluated low-frequency scaling relations for dielectric function. The renormalization group approach for evaluating dielectric functions gives good agreement with literature data.

**USING OF PV - STATE EQUATIONS AND THE CORRELATION  
APPROXIMATION FOR THE INVESTIGATION OF THE  
ELASTIC PROPERTIES OF SOLIDS.**

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The receipt of PV-state equations is the main problem of condensed matter physics. The investigations of PV-state equations were carried out during the last 100 years and to the present time the PV-equations were received for different potential types, which act between atoms and molecules of solids. All these investigations were carried out for the isotropic case and this is correct only for the amorphous solids.

The new approach for the investigation of the elastic properties of crystals, consisted of using of PV-state equations for the establishment of analytical connection between the components of macrostress tensor, the deformation tensor, the change of the crystal volume and quantitative characteristics of atom - atom potential was developed in this work. PV-state equations were received with taking into consideration the crystal anisotropy for the cases of cubic, hexagonal, rhombic and tetragonal crystal symmetry.

To build the statistical crystal theory it is necessary not to neglect the space correlation of its particles movement, because in some cases the neglect leads to the considerable divergence of theoretical and experimental results.. To account the space correlation in the crystal the chain of Bogolubov's equations for the correlation functions (density matrixes) was used. On the basis of the first and second order radial distribution functions the PV-state crystal equation was obtained in the nought and first approaches of the correlation theory correspondingly. The received PV-state equation was investigated by computer simulation methods (Fortran) for the specific atom - atom potential forms (Mi-Grunaisens', Morses', Bukingems' potentials). It was obtained that the correlation correction for the pressure P in PV-state equation is the highest when the attraction index m and the repulsion index n are the lowest (the repulsion index n and attraction index m are the specific characteristics of atom - atom potentials); moreover, the correlation correction decreases with the increase of m and n indexes. The approbation of the present investigation complex was carried out on  $\alpha$ -Ti alloys. It was obtained for  $\alpha$ -Ti that the correlation correction for the pressure P in PV-state equation forms 0.002%-0.005% of the initial pressure. This method can be used not only to  $\alpha$ -Ti alloys, but to all solids, which are described by atom - atom Mi-Grunaisens', Morses' and Bukingems' potentials.

## Nonstationary undulate of magnetization in ultra-dispersion ferromagnetics.

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Theoretically explored possibility to realization an nonstationary spatial turning magnetization under inhomogeneity of local anisotropy. Considered model, where as inhomogeneity emerge cristallites with uniaxial by the anisotropy. Sizes of cristallites, directions of local axes to anisotropy and constants of anisotropy in general event - random quantities portioned on free laws.

On the base univariate flaky models are calculated correlation functions of inhomogeneity at presence (absence) different types of the chaos in the field of anisotropy, structured functions of magnetization (in the event of nonstationary turning) and sizes of areas an quasi-uniform magnetization (blocks).

Realized, equations for equilibrium position of magnetization expect a space nonstationary deciding, which, in principle, can be realized in real material. Analytically shown that structured functions of magnetization uncritical to the profile of correlation functions of inhomogeneity, but are defined in main correlation by the length of inhomogeneity. For models with the different type of disorder in the field of local anisotropy in the event of spatial nonstationary structured functions an aproximate are described by the equation (in the event of the strong exchange in contrast with the anisotropy):

$$Q(x, r) \approx \frac{\langle a \rangle}{\delta_0^4} \left( x r^2 + \frac{1}{3} r^3 \right),$$

for the factor of correlations of magnetization received following expression:

$$K(r) = \frac{1 + 3/2(r/\delta)}{(1 + (r/\delta))^{\frac{3}{2}}}.$$

Here  $\langle a \rangle$  - an average width цноев,  $x$  - a distance from the free edge of the sample,  $r$  - a distance between correlation spins,  $\delta_0, \delta$  - a width of domain wall of uniform material and width of block accordingly.

Modeling of turning of magnetization was conducted on the computer. Quantity experiment completely has confirmed analytically tinned dependencies.

# Efficient anisotropy and spin-orientation transition in ultra-dispersion ferromagnetics.

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Studied magnet with strong ferromagnetic exchange interaction with inhomogeneity in the manner of crystallites. Sample divided on  $N$  crystallites, volumes and directions of local anisotropy's axes (EAM) which random and distributed on free law.

Considered inhomogeneity of different dimensionality: three-dimensional (grain), two-dimensional and univariate (flaky structure). Expressions for efficient constants (with provision for second), as functions of dispersion of volumes of inhomogeneity  $\sigma^2$  and parameters of texture  $\mu$  received by levelling the rotating moments on the part of random field of anisotropy and efficient uniaxial to anisotropy. As a result received following equation:

$$\begin{aligned} K_{1_{\text{eff}}} + K_{2_{\text{eff}}} &= (K_1 + K_2) \sqrt{\frac{1 - \mu_1^2}{N} \left( \frac{\sigma^2}{\langle v \rangle^2} + 1 \right) + \mu_1^2}, \\ K_{2_{\text{eff}}} &= K_2 \sqrt{\frac{1 - \mu_2^2}{N} \left( \frac{\sigma^2}{\langle v \rangle^2} + 1 \right) + \mu_2^2}, \end{aligned} \quad (1)$$

here  $\langle v \rangle$  - an average single-line size an crystallites,  $\mu_1 = \langle \cos(2\alpha) \rangle$ ,  $\mu_2 = \langle \cos(4\alpha) \rangle$  - parameters of texture in directions EAM (angular parentheses mark an operation of averaging).

On the example of event of even sharing the directions of local axes to anisotropy predicted possibility spin-orientation transition between phases "light axis", "angular phase" and "light plane". For the case in point received equations of inter-phases surfaces in the space of parameters  $\sigma^2$ ,  $\chi$ ,  $\alpha_0$ :

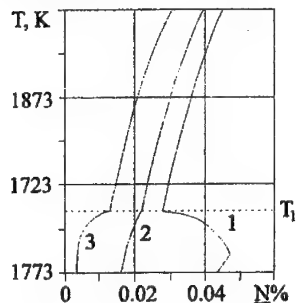
$$\begin{aligned} \frac{\chi_{\text{eff}} + 1}{\chi + 1} &= 2 \sqrt{\frac{(4\alpha_0^2 - \sin(2\alpha_0))(\sigma_v^2 + 1) + 4N \sin^2(2\alpha_0)}{(16\alpha_0^2 - \sin(4\alpha_0))(\sigma_v^2 + 1) + 16N \sin^2(4\alpha_0)}}, \\ \chi_{\text{eff}} &= 0, -1/2, \end{aligned} \quad (2)$$

here  $2\alpha_0$  - an interval of values of angles of fluctuation EAM,  $\chi_{\text{eff}} = K_{1_{\text{eff}}}/K_{2_{\text{eff}}}$ ,  $\chi = K_1/K_2$ ,  $\sigma_v^2 = \sigma^2/\langle v \rangle^2$ .

## SIMULATION OF SOLUBILITY NITROGEN AT PROCESS OF CRYSTALLIZATION MULTICOMPONENT IRON MELTS

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The method of physics-chemical analysis in multicomponent alloys under cooling and crystallization was developed. The method include physical models, mathematical description of their and packet of computer programs.



Change an concentration of nitrogen in alloys Fe-0.05%C-1.0%Cr-0.2%Al-Ti-N when entering Ti (mas.%):  
1 - 0.1%, 2 - 0.13%, 3 - 0.2%.  
x - concentration of N before entering Ti

Computer simulation of cooling of reheat above liquidus of alloys had shown that:

1. Proposed method with the exact account of conservation mass law gives different from accepted method of calculation a result in all interval of temperatures of cooling, including initial isotherm (refer to drawing, initial temperature is 1923 K).

2. Crystallization in connection with microsegregational processes intensifies a shift of equilibrium, changing a composition here take place with an enriching (1), almost monotonous (2), with an impoverishing (3) of liquid. That is mutual influence of components can

cause break of curves and change their motion on opposite.

3. Changing the initial conditions is reached shift of course the chemical reactions in the given temperature interval that is reflected on the quantity and composition of products of reactions, distribution their inside crystals and microsegregation.

Developed method is based on fundamental principles and concepts of thermodynamics, (Gibbs free energy, activity, law of conservation of masses, rolling and local equilibrium of appearing phases and others), applying to unisothermal processes. All this is a further development of metallurgical processes theory and creates a possibility of new approach to the analysis of technical processes of preparation of alloys (deoxidization, desulphurization, degazation and so on), in which crystallizational processes are determined.



### QUANTUM CHEMICAL MODELING OF ORDERING EFFECTS IN POLYTYPES $\text{AlN-Al}_2\text{O}_3$

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The purpose of this work was the theoretical modeling influence of ordering effects upon energy states of concentration polytypes in the system of  $\text{AlN-Al}_2\text{O}_3$  and making attempt to interpret the nature of structural states of concentration polytypes on the basis of band theory.

The effects of oxygen impurities and vacancies ordering in wurtzite polytypes of  $\text{AlN-Al}_2\text{O}_3$  were studied. The total energies, Fermi energy values, total densities of states and overlap population of crystal orbitals were computed with the semiempirical band method on Huckel scheme of matrix elements parametrisation. The calculations were performed using 16-, 32-, 72-, and 144-atomic supercells with various ratios of atoms (Al, N, O) and structure vacancies. The composition of supercells and relational position of different type atoms simulated possible variants of stoichiometric and structural states.

Quantitative analysis of data obtained allowed to conclude following.

- 1) Oxygen impurities, substituting nitrogen atoms, form two-layered planes.
- 2) The two-layered oxygen planes formation is due to electronic interaction character and lattice type, while one is not a result of interaction of oxygen atoms with vacancies.
- 3) There is a interlayer stacking type inversion relatively plane (1,1,0) in the oxygen plane. It results in arising hexagonal ( $2nH$ ) and rhombohedral ( $3nR$ , where  $n$  is integer) polytypes set.
- 4) The local rebuilding of atomic ordering causes modification of aluminum atoms coordination like the characteristic of  $\alpha\text{-Al}_2\text{O}_3$ .

This work is supported by Russian Fund for Fundamental Researches, grant 98-03-32512.

**MATHEMATICAL AND COMPUTER MODELING  
OF HEAT- and-MASS TRANSFER PROCESSES IN COMPOSITE  
FIRE-PROTECTING MATERIALS CONSIDERING THE  
CHANGES OF THEIR PROPERTIES UNDER HIGH-  
TEMPERATURE HEATING**

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Modern fire-protecting materials are compositions based on mineral (cement, gypsum, liquid glass) or organic (polymer) binders decomposing in heating, and thermally stable powder or fibrous fillers. To optimize the composition of fire-protecting materials and to estimate the required thicknesses of fire protection, a mathematical model, adequate to nature, of heat-and-mass transfer in it is needed which allows to consider the effects of high-temperature heating on the properties of its material.

The authors have developed a mathematical model and computer programs to estimate thermophysical characteristics of composite fire-protecting materials in a wide range of temperatures exceeding the range of temperature changes in a fire. The model allows to take into consideration:

- the changes of the initial composition and thermophysical characteristics of the material's components;
- the contact thermal resistance between the components;
- the effects of the binder's thermal decomposition (dehydration) on the composition and thermophysical characteristics of the material.

Numerical solutions for heat-and-mass transfer have been received in structures with fire protection and for the inverse problem of heat-and-mass transfer to determine parameters for matching the accepted mathematical model of fire-protecting functioning with experiments on the test bench by radiant heating. The conditions of fire-protection's work, conservative to changes, have been accepted as matching parameters: those of radiant heat transfer in the pores of the material and those of vapour diffusion in the porous permeable material of fire protection.

Experimental check-up of the developed mathematical model and computer programs made on its basis has been done by comparing the numerical estimations with the data of firing tests for detail specimens of various structures and shapes having fire protection of different types. The check-up has shown their sufficient adequacy to nature and a feasibility of wide practical applications.

## MODIFIED CRITERION OF PLANAR SOLIDIFICATION FRONT STABILITY FOR MULTYCOMPONENT ALLOYS

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Single crystal structure depends strongly on the morphology of solid - liquid interface during solidification. A planar solidification front is used to obtain homogeneous composition over most of the sample. The conditions under which the front is planar was determined by Rutter, Chalmers [1]. In [2] this criterion was extended for application to ternary alloys. In this paper the criterion was modified. It's shown that the constitutional supercooling should be added vectorially.

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**SEMINAR B.**  
**INTERFACE INTERACTION**

**42-74**

## ALUMINUM - LITHIUM ALLOYS WITH SCANDIUM

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Scandium, a promising addition in Al - Li alloys, refines the as-cast grain structure, facilitates the formation of stable subgrain structure in deformed semis, and improves mechanical properties due to the precipitation of the isomorphic with the matrix  $Al_3Sc$  phase.

The effect of scandium on structure evolution in Al - 2% Li, Al - 2% Li - (3 - 5)% Mg, and Al - 2% Li - (0.5 - 4.2)% Cu was studied. In dependence on scandium content in Al - Li alloys, solidification-origin  $Al_3Sc$  particles form rods 30 nm in diameter (at 0.3% Sc, in eutectic) of polyhedrals to 1000 nm in size (at 0.5 - 0.5% Sc, primary particles). In the latter case, one can observe nondendritic fine-grained structure.

At distinct from a eutectic Al - 2% Li - 0.3% Sc alloy, cast alloys containing magnesium show small colonies of scandium-containing eutectic at 3% Mg or fine polyhedral particles at 5% Mg. At usual solidification rates, the solid solution anomalously supersaturated with scandium is formed upon solidification of these alloys.

The eutectic of Al - Li - Cu alloys containing 0.33% Sc shows round-shaped  $Al_3Sc$  particles 10 nm in size that hardly generate elastic stresses in the matrix. This is, apparently, due to the dissolution of copper in this phase that decreases its lattice parameter. During long-term anneals at 500°C and above, copper diffuses out of the phase and phase particles acquire the typical deformation contrast due to elastic stresses.

Deformed and quenched semis exhibit subgrain structure. Sheets from an Al - Li - Mg - Sc alloy with nonrecrystallized structure demonstrate superplasticity.

The introduction of scandium in Al - Li alloys increases the temperatures of metastable phase precipitation and decreases those of stable phase formation.

## FORMATION MECHANISMS OF SELF-REINFORCED SiC- AND AlN-MATERIALS

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Two types of self-reinforced materials are formed during solid phase sintering of SiC with addition of boron and AlN with impurity of oxygen: individual grains are reinforced by plates; plates with aspect ratio  $\geq 10$  grow in the matrix of isometric grains.

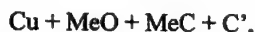
In the work self-reinforcing mechanisms in the materials are proposed on the base of electron microscopy study on the structure evolution during free sintering of SiC (1800-2000 °C) and AlN (1600-2000 °C). Development of these mechanisms is due to following sequence of structure transformations.

1. Formation of solid solutions SiC-B and AlN-O.
  2. Isostructural heterogeneous (with participation of basal stacking faults) delamination of solid solution. The process caused precipitation in the grains of plates faceted by (0001) planes. Such plates are composed by multilayered polytypes (MP).
  3. Formation of centers for growth of plate-like grains owing to abnormal mobility of boundary fragment which separated intragranular MP-layer.
  4. Solid state growth of plate-like grains (abnormal grain growth).
- At the growth of such grains diffusion polytype transformations  $4H \rightarrow 6H$ ,  $6H \rightarrow 3C$  in SiC and  $2H \rightarrow MP$  take place.

SOLID PHASE INTERACTIONS AND THEIR INFLUENCE ON  
STRUCTURE AND PROPERTIES OF OXIDE AND CARBIDE  
DISPERSION STRENGTHENED COPPER OF THE DISCOM®  
TRADE MARK

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The Chuvash State University, Cheboksary, Russia

Oxide and Carbide Dispersion Strengthened Copper (OCDS-Copper) of the DISCOM® trade mark represents in the most cases the following system:



Where: Me is an oxide and carbide forming element;  
C' is exuberant carbon being in free ultradispersible state and acting the role of an additional strengthening phase as well as an antifrictional and antiadhesion addition.

So OCDS-Copper contains three strengthening phases: oxide, carbide and carbon. Metals chosen from the III, IV, V and VI groups of the D.I. Mendeleev's Periodic System of Elements are used as oxide and carbide forming elements. Al, Ti, Cr and V are used more frequently. Therefore  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{VO}_2$ ,  $\text{Al}_4\text{C}_3$ ,  $\text{TiC}$ ,  $\text{Cr}_3\text{C}_2$ , VC are strengthening phases (dispersoids) in industrially fabricated OCDS-Copper.

Phase composition of dispersoids formed in these materials was determined by methods of transelectronic microscoping on thin foils and by methods of X-ray anode deposit analysis got at electrolyte dissolving of materials.

Alloying elements content (for example, Aluminium) in a copper hard solution was determined by the lattice period changing based on Vegart rule. The lattice period was calculated on the corresponding diffractinal lines taken from microsection on points with accurate to 0,0005Å.

The stereological analysis of particles was carried out by methods of E. Shile – G. Shwarz – S.A. Saltykov on the material specimens replicas.

Due to that initial powder mixture and granules got from it in attritors; thermally processed briquettes made of the granules and hot extruded bars as well as bars made of initial powder mixture were subjected to the mentioned investigation it has become possible to find out and describe the main solid phase interactions and a forming process of the base of materials and phases strengthening it as well as influence of these interconnections on structure and properties of OCDS-Copper.

# **PHASE DIAGRAMS OF THE SYSTEMS AL<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-RARE EARTH OXIDES**

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The systems Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-Ln<sub>2</sub>O<sub>3</sub> (Ln - lanthanides) attract considerable attention as a source of materials for structural ceramics as well as for modern fuel cells. The phase diagrams of these systems are very useful for the designers of advanced ceramics. No information about the interaction in these systems is available yet.

The analysis of literature data allowed to conclude that the interactions in the systems Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-Ln<sub>2</sub>O<sub>3</sub> were defined by the interactions in the bounding systems Al<sub>2</sub>O<sub>3</sub>-Ln<sub>2</sub>O<sub>3</sub> rather than in the systems ZrO<sub>2</sub>-Ln<sub>2</sub>O<sub>3</sub>. It allowed to divide all the systems into five groups, in which the interactions were similar. Hence the systems Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-Ln<sub>2</sub>O<sub>3</sub>, where Ln = La, Nd, Sm, Er, Yb, as well as the system Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> were chosen for the experimental research.

The systems under investigation were triangulated and the phase diagrams of the isothermal sections at 1250 and 1650 °C were constructed. The main feature of triangulation is the existence of equilibrium between ZrO<sub>2</sub>-solid solutions and aluminates of lanthanides (LnAlO<sub>3</sub>, Ln<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> and Ln<sub>4</sub>Al<sub>2</sub>O<sub>9</sub>). The formation of superstructures in the bounding systems ZrO<sub>2</sub>-Ln<sub>2</sub>O<sub>3</sub> leads to the appearance of additional tie-lines in the isothermal sections of the systems at 1650 °C (La, Nd, Sm, Yb) and 1250 °C (La, Nd, Sm, Y, Er, Yb).

The total equilibrium phase diagram and metastable phase diagram for the system Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> in the temperature range 1600 - 2800 °C were investigated for the first time. Because of the existence of wide areas of solid solutions in the boundary systems ZrO<sub>2</sub>-Ln<sub>2</sub>O<sub>3</sub> the ternary systems Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-Ln<sub>2</sub>O<sub>3</sub> have only partially quasibinary sections. The interactions in the systems have the eutectic character. The ternary compounds and areas of solid solutions are not found. The last fact is the scientific base for creating composite ceramic materials for structural and functional purposes with increased mechanical properties.



## REACTION OF CARBIDIZATION WITH THE INVOLVEMENT OF GAS PHASE

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The reaction of metal and carbon interaction as the reaction between two solid phases may be referred to the class of solid. However together with known types of interaction between metal and solid carbon as a carbon black or graphite the methods of carbide preparation by reaction of metals with carbon contained gas compound is broad known also. In this work on the example of different systems (Mo-C, W-C, W-Co-C and Mo-W-C) the analysis of change of kinetic parameter under interaction of metal with carbon and the dispersion of the reaction products in dependence of active form of carbon was carried out.

There is found that the solid reaction between metal and carbon is taken place only in flowing inert gas medium and carried out by diffusion interaction. In reduction medium the diffusion interaction and partial conversion of a solid carbon into gas compound with hydrogen and following adsorption on the metal surface with the change in more active forms of carbon is taken place at a time. The reaction rate in this case increases, the temperature interaction may be decrease and the prepared carbon dispersivity increase. The change of solid carbon by carbon contained gas reagent aid to accelerate of interaction between metal and carbon, to reduce the reaction temperature and increase the dispersivity of intermediate and final products.

The reaction of interaction between metal, in particular molybdenum and tungsten, and solid carbon contained organic compound has been defined by phase form of active carbon, prepared as a result of decomposition of these compounds under heating. The most reaction useful in this case is a gas compounds between carbon and hydrogen. The formation of the active surfaces of solid carbon under their decomposition result in small acceleration of interaction with metal and reduce the temperature of reaction beginning, and the preparation a more disperse carbides.

## EXAMINATION OF PHASE- FORMING IN TUNGSTENLESS HARD ALLOYS ON TITANIUM- CHROMIUM CARBIDE BASE

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Tungstenless hard alloys on titanium and chromium carbides base are perspective wear- resistant materials for corrosion- active media. Stability of these materials is determined by the structure and phase constitution of the sintered product.

Different structure states of material determine a wide range of its functional properties. The paper seeks to study the forming conditions of different material structure states of a titanium- chromium carbide- based material of the same composition. It was investigated the alloys phase constitution behaviour in the course of sintering TiC,  $\text{Cr}_3\text{C}_2$  and Co mixture and binary TiC-  $\text{Cr}_3\text{C}_2$  carbide with cobalt in the temperature range from 800 to 1350°C in vacuum.

On heating at a temperature of 800°C in TiC-  $\text{Cr}_3\text{C}_2$ - Co system the chromium carbide  $\text{Cr}_7\text{C}_3$  emerges and hexagonal Co begins to transform into cubic Co and up to the temperature of 1350°C three phases are present in the system- TiC,  $\text{Cr}_7\text{C}_3$  and Co.

In the system with binary TiC-  $\text{Cr}_3\text{C}_2$  carbide and cobalt the TiC- based solid solution remains up to the temperature of 1200°C. When heating is continued beyond 1200°C the solid solution decays to yield chromium carbide  $\text{Cr}_7\text{C}_3$ .

Considering that the active sintering temperature is 1350°C, the binary TiC-  $\text{Cr}_3\text{C}_2$  carbide loses its initial characteristics, decomposes and turns to TiC and  $\text{Cr}_7\text{C}_3$  carbide mixture similar to carbide mixture based system which was investigated before.

The obtained information testifies that after sintering beyond 1200°C there no fundamental differences between phase constitution of the resulting products whether carbide mixtures or solid solutions are the original systems. So the choice of the initial materials for producing such alloys should be economically attractive only.

THERMODYNAMICS OF ALLOY FORMATION IN  
Al-Ge(Si)-Fe(Cu) TERNARY SYSTEMS

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Investigation of thermodynamic properties of ternary aluminium systems with germanium (silicium) and 3d-metal is important in connection with amorphisation processes during rapid solidification study.

The thermodynamic investigation of Al-Ge(Si)-Fe(Cu) ternary systems, that have been performed at physical chemistry department of National Taras Shevchenko University of Kyiv by experimental and calculated methods, shows remarkable negative deviation from ideal solutions.

Comparative analysis of integral mixing enthalpies and Gibbs energies concentration dependencies shows that thermodynamic behaviour of liquid Al-Ge-Fe, Al-Ge-Cu and Al-Si-Cu alloys are similar. Absolute values of  $\Delta H$  and  $\Delta G^{\text{ex}}$  gradually increase from Al-Ge(Si) to Al-Fe(Cu) side. Maximal components interaction is observed in limiting binary systems Al-Fe and Al-Cu, that agrees their with phase diagrams, which are characterized by existence of intermetallic compounds.

The mixing heat concentration dependence in Al-Si-Fe alloys is somewhat another. Extreme  $\Delta H$  values are observed on Si-Fe side. This fact is explained by existence in binary Si-Fe system of thermal stable intermetallic compound FeSi and remaining strong atomic interaction over liquidus line.

This results may be need for glass-forming ability evaluation in ternary aluminium systems.

## INTERFACIAL INTERACTION IN NICKEL-BISMUTH, NICKEL-ZINC AND COBALT-ZINC DIFFUSION COUPLES

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Interfacial interaction in nickel-bismuth, nickel-zinc and cobalt-zinc binary systems was studied using metallography, X-ray analysis and electron-probe microanalysis. The  $\text{NiBi}_3$  intermetallic layer was found to grow between nickel and bismuth at 150 to 250°C and annealing times up to 75 h, the other compound  $\text{NiBi}$  being missing in the Ni-Bi couple. The  $\text{NiBi}_3$  growth kinetics were parabolic, indicative of the diffusion-controlled process. Inert markers (microhardness indentations on the surface of the Ni-Bi cross-sections) showed the bismuth atoms to be the main diffusing species in the course of layer formation.

The layer-growth kinetics in nickel-zinc and cobalt-zinc diffusion couples were much more complicated. Firstly, two intermetallic layers grew at the interfaces in the 250 to 400°C temperature range, though four intermetallics exist in each of these binary systems [1]. Secondly, small deviations from the parabolic relationship were observed.

The diffusional theory predicts the direct proportionality between the width of the range of homogeneity of an intermetallic compound and the growth rate of its layer [2]. In fact, no definite relationship was revealed between these quantities. Moreover, the growth rate of the layer of the  $\text{NiBi}_3$  compound having no measurable homogeneity range in the nickel-bismuth couple turned out to be even greater than that of any of the intermetallic layers in the nickel-zinc and cobalt-zinc couples, although these have homogeneity ranges from 1.5 to 10 at.%. This supports the conclusion of the physico-chemical approach [3] that the existence of a homogeneity range of a chemical compound is not a decisive factor in determining the layer-growth rate.

The reasons for the absence of some intermetallics in the reaction couples investigated and also the results of marker experiments will be discussed in detail.

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## COMPOSITES WITH METAL AND CERAMIC HIGH POROUS CELLULAR MATRIX

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The capabilities of modifying of macrostructure of cellular foam materials by methods combinable with technologies of duplication of polyurethane foams are esteemed.

The modifying included fulfilment of such operations with duplicated cellular structure, as creation of gradient of structural properties in it, introducing or joining to its outside surface of cast or porous elements with desired geometrical configuration.

The suspension, chemical, electrochemical and combined methods of obtaining of composites with high porous cellular matrix are studied, for provision of desired chemical composition, structural - hydraulic, mechanical and thermal properties, disposition of functional elements and overall dimensions of produced specimens.

It is established regularity of formation of contact' zone between components of cellular metal and ceramic matrix and affixed to it similar functional elements depending on conditions of process of coatings' deposition on duplicated polymer substrate.

# PHASE TRANSMISSION IN TALLIUM CHALCOGEN-HALLOGENIDES TERNARY SYSTEMS

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The paper studies the results of phase transmissions investigation of TlSe-TlCl-TlBr (I), TlSe-TlCl-TlI (II) and TlSe-TlBr-TlI (III) systems using the differential thermal analysis (DTA) and X-ray diffraction. Same politermic cuts were plotted. the regions of primary crystallisation, the coordinate of non- and monovariantic transmission were established.

The alloys for phase transmission investigation were prepared by melting of disired propotion of binary TlSe and thallium(I) chalcogenides and hallogenides under vacuum (0,133 Pa) in quarts tubes. The mixture were molten (the maximal temperature was 763 K) and then annealed for period 168 hours (the temperature was 483 K).

The system (I) are characterised by monovariantic eutectic equilibration  $L \rightleftharpoons \alpha + \beta$ , which goes in the appropriate temperature range 605–595 K. In the ternary system  $\alpha$ -solid solutions are formed on thallium (II) hlorides and bromides base,  $\beta$ -limite solid solutions – on the thallium selenides. The base of ternary system are formed by two binary eutectic type systems: TlSe-TlCl (eutectic is drawing up at 605 K from TlSe side), TlSe-TlBr (eutectic is crystallise at 595 K and locate at 10 mol.%TlBr) and TlCl-TlBr binary system, which characterised by unlimited liquid and solid solutions in the all concentration region. The phase relations in the system (II) is discribe by the nonvariantic diagrafe type:  $L \rightleftharpoons \alpha + \beta + \gamma$ . The lines of monovariantic equilibrations, which limited the region of  $\alpha$ -(base on TlCl),  $\beta$ -(base on TlSe) and  $\gamma$ -(base on TlI) solid solutions primary crystallisation are crissed at the ternary eutectic point E ( $\approx 530$  K,  $\approx 46$  mol.%TlSe, 10 mol.%TlCl, 44 mol.%TlI). The phase diagrafe of ternary system (III) belongs to monovariantic eutectic equilibration  $L \rightleftharpoons \alpha + \beta$  (goes in the appropriate temperature range 595-538 K). The  $\alpha$ -solid solutions are formed on the TlBr and high-temperature TlI modifficatin components,  $\beta$ -limite solide solution - on the TlSe compounds. Eutectic in the TlSe-TlBr binary systems are located at 10 mol.% TlBr (595 K) and in the TlSe-TlI binary system – at 50 mol.%TlI (538 K). The investigations of phase relations was established that the new complex compounds in this ternary systems are not formed.

INTERPHASE INTERACTION AND STRENGTH  
OF TITANIUM-NIOBIUM-COPPER FIBROUS COMPOSITE  
UNDER THE THERMAL EFFECT

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The relationship between the strength properties of a composite material and the change of diffusion layer and intensification of the processes of physico-chemical interaction of the components under the temperature effect, as well as the role of the reinforcing fibre physical state, their dispersity and dispersity of the composite material structure as a whole have been investigated in the paper.

The objects for the investigation were the high-dispersed composite materials based on reinforcing fibres of titanium-niobium alloy and matrices from copper and its alloys. The cold-worked samples, 0,35 - 0,50 mm in diameter, contained 44521 continuous longitudinally oriented reinforcing fibres of 0,85 - 1,2 m diameter. The content of reinforcing fibres by volume was equal to 22,5 - 26 %. The total extrusion ratio  $\sim 10^9$ .

It has been found that with the activation of the interphase interaction processes and increase of the temperature of annealing the lowering of the longitudinal strength is typical of the composite with matrix from nickel-copper and manganese-copper alloys.

For the composite with matrix from copper the typical is the monotonous growth of longitudinal strength influenced by the interaction products. The high-disperse composite possesses the experimental strength which is 30 - 50 % higher than the calculated by the additivity rule.

When developing and operating the composite with reinforcing fibres based on Nb-Ti alloy and matrices based on copper and copper alloys the temperature boundary within the limits of 250 - 400 °C was specified.

## CONTACT INTERACTION OF REFRACTORY MATERIALS WITH BASALT MELT AND DEVELOPMENT OF CORROSION-RESISTANT COMPOSITES.

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Nowadays the fibres and materials on the base of basalt obtained from the natural raw material find a wide application. The study of contact interaction of basalt with refractory compounds to develop the new ceramics of "refractory compound-basalt" system and elaborate the composite materials stable in a liquid basalt for the draw plates being used for the fabrication of basalt fibres is of a great interest.

The investigations of a wetting of refractory materials on the base of borides ( $\text{TiB}_2$ ,  $\text{ZrB}_2$ ,  $\text{TiCrB}_2$ ,  $\text{LaB}_6$ ), nitrides ( $\text{AlN}$ ,  $\text{BN}$ ,  $\text{Si}_3\text{N}_4$ ) and silicides ( $\text{MoSi}_2$ ,  $\text{WSi}_2$ ) with liquid basalt were carried out. The contact wetting angles were determined. It was shown that a majority of materials above are wetted by liquid basalt, the contact angles being  $< 90^\circ$ .

The detail analysis of phase composition in the interaction zone was carried out. It was established that both  $\text{WSi}_2$  and  $\text{MoSi}_2$  as well as materials of  $\text{MeB}_2$ - $\text{MeSi}_2$  system are not practically wetted by liquid basalt, these materials having a high chemical resistance in a basalt melt.

Among the materials investigated the refractory borides, silicides and materials on their base as well as materials on the base of non-metallic nitrides ( $\text{BN}$ ,  $\text{Si}_3\text{N}_4$ ) with the additives of electroconductive materials may be recommended as high-resistant materials stable in the basalt melt.



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**Hightemperaturestrength the fibre-reinforced composite materials on a basis of Chromium.**

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The results theoretical both experimental researches on development and test of composite materials, reinforced by the fibres W and SiC. The report consists of three sections. First is devoted to computer modeling of processes of deformation and destruction FCM of the chosen systems and estimation of their properties. The second section - theoretical and experimental research of processes of physico-chemical interaction in samples FCM and development of technological bases of reception of composites. In last section the results of research of structure and properties FCM in wide (up to 1400 C) an interval of temperatures are resulted

# NEW THERMOELECTRIC COMPOUNDS IN $\text{Ti}_2\text{C}^{\text{VI}}-\text{B}^{\text{IV}}\text{C}^{\text{VI}}_2$ ( $\text{B}^{\text{IV}}-\text{Ti}, \text{Zr}; \text{C}^{\text{VI}}-\text{S}, \text{Se}, \text{Te}$ ) SYSTEMS

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The phase relations in  $\text{Ti}_2\text{C}^{\text{VI}}-\text{B}^{\text{IV}}\text{C}^{\text{VI}}_2$  ( $\text{B}^{\text{IV}}-\text{Ti}, \text{Zr}; \text{C}^{\text{VI}}-\text{S}, \text{Se}, \text{Te}$ ) quasibinary systems have been investigated previously [1,2]. The  $\text{Ti}_4\text{B}^{\text{IV}}\text{C}^{\text{VI}}_4$ ,  $\text{Ti}_2\text{B}^{\text{IV}}\text{C}^{\text{VI}}_2$ ,  $\text{Ti}_2\text{B}^{\text{IV}}_2\text{C}^{\text{VI}}_5$  types compounds have been found. The homogeneous regions were established to them.  $\text{Ti}_4\text{TiS}_4(\text{Se}_4, \text{Te}_4)$ ,  $\text{Ti}_2\text{Ti}(\text{Zr})\text{S}_3$  and  $\text{Ti}_4\text{ZrS}_4$  are melt congruently. The aim of the study to determine some physico-chemical and electrophysical properties of ternary thalious(I)-titanium(IV)(zirconium(IV))-chalcogenides.

Compounds were prepared from the proper amounts of high purity thalious(I) chalcogenide and elemental titanium(zirconium) and chalcogenide in evacuated to 0.13 Pa quartz tubes by special developed technological regimes, according to phase diagrams. The possible mechanism and dissociation parameters (degree and constant) by melting have been proposed and calculated. The melting entropy and enthalpy have been established. The high thermal stability have been shown to  $\text{Ti}_4\text{ZrS}_4$  ( $\alpha_{\text{dec}}=0.04$ ),  $\text{Ti}_4\text{TiS}_4$  ( $\alpha_{\text{dec}}=0.26$ ),  $\text{Ti}_2\text{TiS}_3$  ( $\alpha_{\text{dec}}=0.20$ ). The  $\text{Ti}_4\text{TiS}_4(\text{Se}_4, \text{Te}_4)$ ,  $\text{Ti}_2\text{TiS}_3$  и  $\text{Ti}_4\text{ZrS}_4$  single crystals growth by Bridgman technique. Some electrophysical properties were studied to crystals (table 1).

Table 1. Properties of  $\text{Ti}_4\text{TiS}_4(\text{Se}_4, \text{Te}_4)$ ,  $\text{Ti}_2\text{TiS}_3$  and  $\text{Ti}_4\text{ZrS}_4$  compounds.

Compound	T K	Homogeneous region	$\Delta H$ , kJ/mole	$\Delta S$ , J/mole·K	$\rho$ , ohm·cm	$\Delta E_a$ , eV	thermo-EMF, mV/K
$\text{Ti}_4\text{TiS}_4$	798	2,5 mol. %	117,2	147,3	$7 \cdot 10^7$	1,1	1120
$\text{Ti}_4\text{TiSe}_4$	780	5,0 mol. %	84,2	107,6	$7 \cdot 10^8$	0,3	150
$\text{Ti}_4\text{TiTe}_4$	878	3,0 mol. %	121,1	137,9	$10^2$	-	100
$\text{Ti}_2\text{TiS}_3$	812	3,5 mol. %	136,2	167,7	$7 \cdot 10^2$	0,1	6000
$\text{Ti}_4\text{ZrS}_4$	985	10,0 mol. %	42,95	43,60	$10^4$	0,8	600

The high thermo-EMF of some single crystals have been found. Its shows their perspective as thermoelectric elements.

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## SiC FIBER/TI ALLOYS COMPOSITE

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Application of Ti alloys is promising for gas turbines production of modern flight apparatus and they push out successfully thermostability superalloys presently used for this purpose [1].

For the extension of service temperature range of the gas turbine parts recently numerous R&D Ti-based composite have been carried out [2-3].

One of the problems of creation SiC fiber/Ti alloy composites is the interaction of the reinforcing fiber and matrix during the development and service of material that leads to the material strength decrease.

The prevention (decrease) of the fiber/matrix interaction reached by barrier layers deposition on fiber and matrix alloying.

The method of obtaining composite of pure Ti and Si riched Ti alloy matrix and SiC fiber composite was investigated in this work. Hot pressing (static and dynamic) method of the powder materials was used. The cross-section investigation of two types of composites showed that the fiber/matrix zone of the interaction for Si-riched Ti alloys is less than that for pure Ti alloy.

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# INTERPHASE INTERACTION IN THE $\alpha$ -, $\beta$ -SiC - Si - Cr - Fe SYSTEM

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The analysis of the process of the interphase interaction in the disperse system and ceramics based on  $\alpha$ - and  $\beta$ -SiC with additions of Si, Cr, and Fe are investigated by using a complex of methods of physicochemical investigations at different stages of their treatment, namely, during joint grinding in a high-speed steel mill, temperature treatment of the disperse system in the temperature range 1400-1600°C in argon, and pressing of samples under a pressure of 5 GPa at a temperature of 1800°C.

It is found that in the course of joint grinding traces of chromium and iron silicides appear. The content of silicide phases increases during further temperature treatment. The phases CrSi and FeSi<sub>2</sub> prove to be dominant in the  $\alpha$ -SiC - (Si + Cr + Fe) (I) system, and phases Cr<sub>3</sub>Si and FeSi<sub>2</sub> are dominant in samples based on  $\beta$ -SiC - (Si + Cr + Fe) (II). The difference in phase composition between samples I and II is due to macrononuniformity of the distribution of Cr, Fe, and Si through the volume of powder and of SiC particles at the stage of mechanical treatment specified by the particle size, degree of their aggregation, and hardness.

During pressing of samples under high pressures, the  $\alpha$ -SiC  $\rightarrow$   $\beta$ -SiC transformation takes place, all diffraction lines broaden considerably, graphite-like carbon and phases of iron and chromium carbosilicides appear. The obtained ceramics is characterized by high dispersity of the structure.

**DIRECT STUDY (IN SITU) OF INTERPHASE COOPERATION  
IN TWO-LAYERED CONDENSATE Ni-Ag DURING  
HEATING UP TO 900°C**

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The study of structural changes of Ag condensative film during heating and melting were carried out by the methods of high-temperature diffraction and transmission electron microscopy in vacuum  $2 \cdot 10^{-3}$  Pa. The choice of indicated metal is connected with absence of oxide films at temperature  $\geq 190^\circ\text{C}$ . The Ni condensate was used as base. Liquid Ag is low-soluble in solid and liquid Ni. The thickness of Ni film was 40 nm according to calculation and of Ag film – 20 nm. The electron diffraction pattern of initial two-layered sample contains lines of Ni and Ag.

At  $750^\circ\text{C}$  the mass-transfer of metal, formation of holes and consolidation of micro-grains take place in Ni film. In the Ag film the coagulation processes and orientation ordering of clusters are observed. Data on Ag agree with the results of work [1]. The coagulation process testifies about liquid-fluidity of Ag. During heating up to  $900^\circ\text{C}$  the amplification of mobility of micro-drops, theirs coagulation and disappearance of separate islands place of observation take place. The character of diffraction maximums of electron diffraction patterns testifies about micro-crystal building of contents of drops-islands.

After cooling film of Ni reminds "scrap" or "sieve" in miniature on the surface of which the ordered, stretched nano-islands of Ag settle down. The electron diffraction pattern from Ni consists of separate shaped reflexes situated on the ring and electron diffraction pattern from Ag consists of broadening circular lines. In area of lines (111) and (200) rings overlap one another from inside. The observed processes interpret with attract of develop by authors representations about structural unstability of crystals at excess of Debay temperature ( $\geq 1,5 T_D$ ) and in the frames of domen-dissipative model of melt's building [2].

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# THERMODYNAMICS OF COMPONENTS INTERACTION IN Ge(Al,Si)-Ga-Gd TERNARY LIQUID ALLOYS

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The rare-earth metals and their alloys are the perspective source of new metallic materials with particular magnetic and electrophysical properties.

In this work mixing heats in whole concentration range for ternary systems Ge(Al,Si)-Ga-Gd were calculated for the first time using the "surrounded atom" model and experimental values in limited concentration ranges.

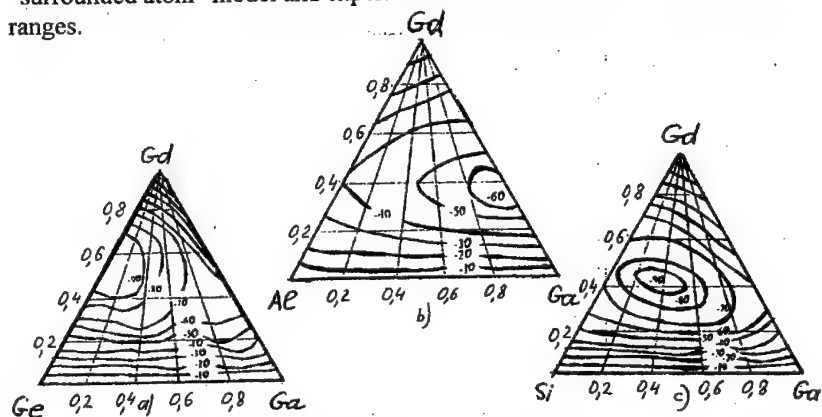


Fig. Integral mixing enthalpies in Ge-Ga-Gd at 1758 K (a), Al-Ga-Gd at 1759 K (b) and Si-Ga-Gd at 1750 K (c) systems calculated by "surrounded atom" theory, kJ/mol.

Calculated results are compared with experimental data from phase equilibriums in these ternary systems.

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# INVESTIGATION OF COMPONENTS INTERACTION ENERGY IN TERNARY Al-Ge-Fe SYSTEM

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There is literature information about possible existence of amorphous alloys in Al-Ge-Fe system [1].

In this report the results of electrochemical investigation of alloy formation thermodynamics in this system, which have been obtained for the first time, are presented.

The values of thermodynamic activities and partial Gibbs energies, entropies and enthalpies for aluminium have been determined from EMF of concentrational cells  $(-)Al_1 | AlCl_3 \text{ in liquid } KCl+NaCl | (Al-Ge-Fe)_1 (+)$  and their temperature coefficients at 1073-1223 K. The integral thermodynamic properties were calculated from partial values by Darken's method.

It has been established that liquid Al-Ge-Fe alloys are characterised by essential negative deviation from ideal solutions, which decrease with temperature growth. It has been shown, that  $\Delta G^{ex}$ ,  $\Delta S^{ex}$  and  $\Delta H$  values become more negative with iron content increase. This fact leads to conclusion about increasing of atomic regulation with Fe content growth.

Besides of experimental investigations  $\Delta G^{ex}$  values in whole concentration range were also calculated using thermodynamic data for limiting binary systems by Bonnier-Cabo method.

It has been shown that thermodynamic properties of liquid Al-Ge-Fe alloys to a considerable extent are determined by atomic interaction in binary Al-Fe system.

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PHASE FORMATION AT INTERACTION OF  $\text{Si}_3\text{N}_4$   
with  $\text{AlN}$  and  $\text{TiN}$

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Metal-ceramic materials on the basis of silicon nitride, particularly SIALONS (Si-Al-O-N) are appropriate materials for extremal conditions to improve their mechanical characteristics hardening additions are used. One of them is titanium nitride  $\text{TiN}$ . To reveal the factors promoting special properties of the composites, the careful examination of components interaction during formation of the composite is necessary.

The present work is aimed to study phase formation processes in the composites of  $\text{Si}_3\text{N}_4$ - $\text{AlN}$ - $\text{TiN}$  subsystem during not pressing. By the methods of DTA, X-ray, EMPA it was shown that  $\text{AlN}$  both with  $\text{Si}_3\text{N}_4$  and with  $\text{TiN}$  in these conditions form stable two-phase equilibria. The defining role here is played by  $\text{Si}_3\text{N}_4$  with  $\text{TiN}$  interaction. Thus, when heating the mixtures  $\text{Si}_3\text{N}_4$ + $\text{TiN}$  and  $\text{Si}_3\text{N}_4$ + $\text{TiN}$ + $\text{AlN}$  first partial (from  $1600^\circ\text{C}$ ), and then complete ( $1902^\circ\text{C}$ ) decomposition of silicon nitride occurs, resulting in free silicon appearance. During the further process interaction of part of silicon with  $\text{TiN}$  takes place leading to  $\text{TiSi}_2$  formation. Presence of  $\text{Si}$ ,  $\text{TiSi}_2$  and  $\text{TiN}$  in the composites results in eutectic equilibria  $L_1 \rightleftharpoons \text{Si} + \text{TiSi}_2$  ( $1280^\circ\text{C}$ ) and  $L_2 \rightleftharpoons \text{TiSi}_2 + \text{TiN}$  ( $1320^\circ\text{C}$ ). Eutectic melts leads to natural densification of the composites during their sintering, and thus, to improving some mechanical characteristics.



## INTERACTION OF BORON CARBIDE WITH MANGANESE, IRON, AND NICKEL OXIDES

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The control of the processes of preparation of borides and composite materials based on them by the process of carboron reduction of oxides requires a knowledge of the mechanism of these processes. Whereas the interaction of  $B_4C$  with oxides of transition metals of the IV-VI groups has been adequately elucidated in the literature, the evidence on the interaction of boron carbide with oxides of metals of the VII and VIII groups are not available.

The aim of this work is to investigate the processes of interaction of boron carbide with manganese, iron, and nickel oxides in the temperature range 800-1800 °C.

Solid products of reactions were characterized by the data of X-ray analysis and, selectively, either by chemical or by petrographic analysis. The composition of the gaseous phase was determined by the mass-spectrometric method. The analysis of chemical transformations in the B-C-O-Mn, B-C-O-Fe, and B-C-O-Ni systems in the considered temperature range was performed by the method of thermodynamic simulation with the use of the «Astra» computer program.

The performed investigations showed that the formation of boride phases began even at temperatures  $\leq 800$  °C. At the same temperatures and up to 1100 °C the borates of the corresponding metals are detected, while in the  $B_4C$ - $MnO_2$  system besides them  $\alpha$ -Mn are also identified. As the temperature grows, along with boron oxides, namely  $B_2O_3$  and  $B_7O_3$ , lower borides and carbides of the corresponding metals, that are dominant in solid products of reactions, are detected. In the gaseous phase CO, vapors of the metals, and molecules of boron oxides are present. It was noted that in the process of reduction under conditions where carbon was deficient, boron began to play a more active role.

The obtained experimental data indicates that, technologically, it is difficult to obtain a pure boride phase of a calculated composition. This is likely attributable to the fact that there exists the large number of stable boride phases with close boron contents and values of enthalpy of formation. The single-phase higher manganese, iron, and nickel borides were obtained at temperatures of 1700-1800 °C and prolonged isothermal exposures.

## INTERFACIAL INTERACTION OF ALUMINIUM WITH TRANSITION METALS AND THEIR ALLOYS

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Interaction of aluminium (either solid or liquid) with transition metals and their alloys results in the formation of intermetallic layers at the Al-Me interface. These are usually very brittle and, if thicker than 2-5 micrometres, strongly deteriorate the mechanical strength of the aluminium-to-metal contact zone. Knowledge of main features of the layer-growth kinetics is therefore of importance in joining the dissimilar metals and manufacturing the aluminium-matrix composites reinforced with fibres of transition metals or their alloys.

Though most of aluminium-transition metal binary systems contain three to eleven intermetallic compounds [1], one or two layers are known to grow at the Al-Me interface at a time, in accordance with physico-chemical views [2]. The first phase to occur is in 70-75% of cases the most Al-rich intermetallic compound. Exceptions are for example binary systems with Fe and V. The initial phase formation, temperature of occurrence, growth morphology and main diffusing species will be discussed.

If a solid transition metal reacts with molten aluminium, the rate of its dissolution in the liquid phase strongly affects the rate of layer growth. By choosing appropriate dissolution conditions, in many cases it is possible to reduce the intermetallic layer thickness to the permissible value. Examples will be presented showing how to calculate the thickness of the intermetallic layer growing under conditions of its simultaneous dissolution in the liquid phase.

If an alloy of transition metals is used, the layer thickness is usually less compared to the cases of pure transition metals. A few examples (Fe-Ni alloys, 18Cr-10Ni stainless steel, etc.) will be treated in detail.

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### CARBOTHERMAL SYNTHESIS OF THE SiC-AIN SOLID SOLUTION

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The nitridation of the mixtures of the silicon and aluminum oxides with soot have been investigated. The mixtures of  $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\alpha$ -quartz as well as  $\gamma$ - $\text{Al}_2\text{O}_3$  and amorphous silicon oxide have been used as raw materials. The ratio of oxides in the mixture varied over a wide range. At the same time the total sum of those made up 70 % by weight. The amount of carbon made up 30 wt.%, that is necessary for nitrides to form by the reaction of carbothermal reduction. The nitridation has been carried out in the nitrogen flow in the temperature range of 1500 – 1800 °C.

It was found out that on using the mixtures of the oxides the formation of nitride phase shifts to the higher temperatures as compared to the nitridation of single oxide. Thus, the nitridation of  $\gamma$ - $\text{Al}_2\text{O}_3$  or  $\alpha$ -quartz at 1500 °C resulted in the formation of the nitrides (AlN or  $\text{Si}_3\text{N}_4$  respectively) with practically 100% yield, whereas after the nitridation of the mixture of those at the same temperature, the nitrogen concentration in the reaction products did not exceed 3,5 wt.%. In this case the main phases were the unreacted oxides. The use of the amorphous silicon oxide accelerates the formation of the nitride phases, however in this case their yield at 1500 °C was also low. The active interaction in these systems took part at 1700 – 1800 °C. In this case according to the X-rays spectra the mixture of the solid solutions of AlN in SiC with concentration up to 15 wt.% and SiC in AlN with concentration up to 7 wt.% was the product of the nitridation. The solution of AlN in SiC resulted in the formation of  $\alpha$ -SiC of wurtzite structure. On using amorphous silicon oxide the SiC-based solid solutions are formed at the lower temperatures.

In accordance with the data of electron microscopy the solid solutions on the SiC basis arise in the form of the fibers with length up to 100  $\mu\text{m}$  and diameter from 0,1 to 5  $\mu\text{m}$  as well as the grains of equiaxial of 0,1-0,3  $\mu\text{m}$ . The solid solutions on the AlN basis are formed only as coarse grains (up to 3  $\mu\text{m}$ ).

## INVESTIGATION OF NITRIDATION AND DEVELOPMENT OF NITRIDE POWDERS BASED ON TI-AL SYSTEM

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Previous investigations of the TiN-AlN composite powders developed from initial TiN and AlN by mixing and hot pressing showed the maximum level of physicomechanical properties corresponded to the stoichiometric  $\text{Ti}_3\text{Al}$ , TiAl and  $\text{TiAl}_3$  intermetallics. Two alternative processes of nitridation were used: nitration of intermetallics themselves and preparation of nitrides from the carbothermally reduced oxides. The obtained results and peculiarities of these processes are discussed below.

The initial intermetallics were arc-melted and then pounded in liquid nitrogen. Fine powders of  $\text{TiO}_2$  (anatase and rutile-modifications),  $\gamma\text{-Al}_2\text{O}_3$  and soot were mixed in the planetary mill and used as initial substances for carbothermal synthesis. Nitridation of intermetallics and oxides mixtures was carried out in a purified nitrogen flow at 1200-1450 °C. The nitrogen flow velocity was 0,5 l/min. The duration of isothermal exposure was from 1 to 6 h.

The phase composition of the reaction products was investigated by the chemical analysis and XRD-method in  $\text{CuK}_\alpha$ -radiation using a "DRON-2" diffractometer. The morphology of the nitride powders was studied by EPMA method.

It was established that  $\text{Ti}_3\text{Al}$ , TiAl and  $\text{TiAl}_3$  intermetallics nitridation realizes in different ways. The nitrogen content change depends on the temperature and increases at high temperatures. All kinetics curves can be described by the parabolic law. Nitride formation rate is limited by diffusion process on the gas solid boundary.  $\text{Ti}_3\text{Al}$  and TiAl nitridation is active enough even at 1200 °C. Complete nitridation takes place at 1400 °C after 3h. Only TiN and AlN nitrides were observed in the reaction products, and at first titanium nitride forms.  $\text{TiAl}_3$  nitridation is rather different. It proceeds very slowly, and complete nitridation was not achieved under the conditions described above. The amount of  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  oxides used for synthesis brings to the formation of nitrides TiN and AlN with ratio TiN:AlN from 3:1 to 1:3 in the reaction products.

It was established that TiN formation begins at 1200 °C when rutile was used as the initial phase. Titanium oxide completely turns into nitride at 1300 °C, but aluminum nitride formation process finishes at 1450 °C and 5 h exposure. The AlN lattice parameters change let us discuss the (Ti, Al)N limited solid solution formation. If anatase was used as the initial phase only TiN (its lattice parameters are close to the standard ones) and  $\alpha\text{-Al}_2\text{O}_3$  were identified in the reaction products.

CHARACTERISTICS OF THE RARE EARTH OXIDES  
THIN FILMS CRYSTALLISATION ON THE AMORPHOUS  
SiO<sub>2</sub> LAYERS SURFACE

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The investigation of structures of SiO<sub>2</sub>- R<sub>2</sub>O<sub>3</sub> (R<sub>2</sub>O<sub>3</sub> - rare earth metals oxides) multilayer system present great interest their outlook as a lightening coatings, UV- laser mirrors, interference filters.

It is known, that for the systems with strong interaction and little discrepancy of lattice parameters the intermediate pseudomorphous layer is forming on the border of the substrate - film, in which the deposit is coherently conjugated with the substrate and the discrepancy is abolished by the uniform film deformation. In the present work the theoretical thickness of pseudomorphous R<sub>2</sub>O<sub>3</sub> layer was calculated and compared with the experiment for scandium, yttrium, erbium and holmium oxides thin films. Under depositing of the abovementioned films on the SiO<sub>2</sub> substrates heated up to 50 - 280°C the formation of quasiamorphous structure was observed. With the temperature increasing the first diffraction maxima appeared, which pointed out the definite advantageous growth to direction in which interatomic distances in R<sub>2</sub>O<sub>3</sub> coincided or were closed to that in SiO<sub>2</sub> on the surfaces border. The formation of the cubic C-form was observed under the condensation of yttrium, erbium and holmium oxides, whereas for the scandium oxide deposition at low crystallisation temperature the two phases were observed. They were cubic and high temperature monoclinial structures. With the condensation temperature increase ( T > 340 °C ) the maxima corresponding the monoclinial phase were disappearing.

The little value of the light dispersion of rare earth oxides thin layers (the package of 20-25 interchanging layers of SiO<sub>2</sub> and R<sub>2</sub>O<sub>3</sub> has the light dispersion less than 0,001% at the wave length  $\lambda = 630$  nm) may be explained by the presence of pseudomorphous structure in the rare earth oxides thin layers.

The rare earth oxides films had high transparency in the visible and near infrared (up to 10  $\mu$ m) spectrum region. Beginning from 10  $\mu$ m the film transmission somewhat lowered and for 400-700  $\text{cm}^{-1}$  the noticeable absorption bands appeared, which corresponded to R-O bond oscillations.

The indexes of refraction of R<sub>2</sub>O<sub>3</sub> thin films were near the refractive indexes of these compounds single crystal in accordance with the published data.

# **CERMETS ON THE TITANIUM CARBONITRIDE BASE WITH TiNi-BINDER: PHYSICAL CHEMISTRY, TECHNOLOGY, PROPERTIES**

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One of the most important problems in the improvement of cermets on the titanium carbide, titanium nitride or titanium carbonitride base is the increase of the strength and toughness of these composites. To solve this problem it was suggested to replace the Ni-Mo-binder of cermets by intermetallic compound TiNi[1].

In this report the results of investigation of alloys on the titanium carbonitride base with TiNi-binder are presented. A number of experiments was carried out, including investigation of the phase equilibrium in  $\text{TiC}_{0.5}\text{N}_{0.5}$  - Ti - Ni - system and influence of some elements (zirconium, vanadium, niobium, molybdenum) on the phase formation in above system, determination of the microstructure parameters of cermets under consideration, measuring of mechanical properties of alloys with various contents of binder.

In particular, it was shown, that the quasi-binary cross-section of the  $\text{TiC}_{0.5}\text{N}_{0.5}$  - Ti - Ni - system is formed by  $\text{TiC}_{0.35}\text{N}_{0.35}$  - TiNi - ray [2]. It was revealed also that the phase composition and structure of considered alloys containing doping elements are more complex than those of industrial TiC ( $\text{TiN}$ ,  $\text{TiC}_x\text{N}_y$ )- Me<sup>VIA-VIA</sup> C-Ni(Mo)-cermets. In the case of considered alloys two- or three-phase structure containing titanium and(or) titanium-alloyed metal carbonitride(carbide) and TiNi-binder is formed if only doping elements with higher or equal affinity to non-metals ( $\text{C}$ ,  $\text{N}_2$ ) in comparison with affinity of titanium to carbon and nitrogen are used. If this condition is not held some intermetallics compounds as  $\text{Nb}_2\text{Ni}$ ,  $\text{Ni}_2\text{V}_3$  or solid solution (Mo(Ti)) are present in cermets besides mentioned phases. On the base of results obtained the manufacturing technology of  $\text{TiC}_{0.35}\text{N}_{0.35}$  - TiNi-cermets in the laboratory has been developed.

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THE STABILITY OF STRUCTURE STATES OF Al-Mg, Al-Li-Mg  
ALLOYS ALLOYED BY Sc, Zr, and Hf

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Low-strength and thermal nonstrengthening Al-Mg alloys 5xxx type are transformed in middle-strength alloys due to alloying their by Sc. During cooling down the ingots of these alloys with the rate about 1-10 °C/s the abnormal supersaturation of the solid solution by Sc takes place. The stable coherent high-strength  $\text{Al}_3\text{Sc}$  precipitate phase ( $\text{L}1_2$  structure) is formed during aging the alloys with Sc. At the same time the metastable ordered ( $\text{L}1_2$ )  $\text{Al}_3\text{Zr}$  phase is precipitated in alloys with Zr.

The main aim of this work was the investigation of aging processes in Al-Mg-Zr alloys with higher Zr composition (0.3, 0.6, 1.0 wt.%). For preparing these alloys the cooling rate 10 °C/s was used. The supersaturation by Zr in Al-Mg-Zr alloys was observed as well as in Al-Mg-Sc ones by Sc. For comparing the efficiency of precipitation of  $\text{Al}_3\text{Sc}$  and  $\text{Al}_3\text{Zr}$  phases on the mechanical properties and structure states stability the Al-4.5%Mg-0.1%Sc and Al-4.5%Mg-0.5%Zr were prepared. In these ones the volume fraction of the  $\text{Al}_3\text{X}$  ( $\text{X}=\text{Sc}, \text{Zr}$ ) precipitates was the same (about 0.4 %). It was founded that  $\text{Al}_3\text{Zr}$  particles drag the grain size growth in cast and deformed states more effectively and the coherent  $\text{Al}_3\text{Sc}$  particles strength the matrix more effectively due to static distortions. The complex alloying of these alloys by Sc, Zr and Hf shifts the interval of  $\text{Al}_3\text{X}$  ( $\text{X}=\text{Sc}, \text{Zr}, \text{Hf}$ ) phase existing to higher temperatures. So, the changing Sc/Zr relation could shift this interval on 100 °C. Moreover the alloying the alloy by Zr could delay the growth rate of  $\text{Al}_3(\text{Sc}, \text{Zr})$  particles.

Alloying the Al-4.5%Mg-0.16%Sc by Li leads to the following effects:

- i- the thermal region of coherent phase  $\text{Al}_3\text{Sc}$  existing grows essentially,
- ii- complex phases  $\text{Al}_3\text{Sc}/\text{Al}_3\text{Li}$  are formed during low-temperature aging,
- iii- these phases drag the coalescence of the metastable  $\delta'$  ( $\text{Al}_3\text{Li}$ ) precipitates, change their size distribution and expand the temperature interval of their existing.

The general regularities of Al-Li-Mg alloys strengthening at complex alloying by Sc+Zr were discussed.

# INFLUENCE OF PHASE HETEROGENEITY & INTERFACE STRUCTURE ON SHRINKAGE & COERCIVITY OF SINTERED PERMANENT MAGNETS BASED ON $\text{SmCo}_5$ POWDERS

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The purpose of the paper is to study the regularities of the shrinkage during sintering of alloys based on  $\text{SmCo}_5$  powders, to elucidate the interface effects upon consolidation of powder particles to find out interconnection between these processes and coercivity of sintered permanent magnets (SPM) and to give some technological remarks on the ground of microstructure analysis and magnetic measurements so that to obtain high coercivity and thermostable SPM.

It was shown in [1,2], that on the stages of the powder pressing and preliminary thermomechanical treatment (before sintering) the following processes take place: (a) the milling of the powder up to the particle size  $\approx 7\mu\text{m}$ , protects the particle against arising the continuous thick oxide films on its surface of; (b) the pressing and thermal treatment at  $T < 200^\circ\text{C}$  may be realized without protection atmosphere, as there are no oxidation reactions and phase transformations in the system; (c) for the alloys of substoichiometric compositions the precipitation of the softer magnetic  $\text{Sm}_2\text{Co}_{17}$  phase on the grain boundaries of the main  $\text{SmCo}_5$  phase are observed. With the increase of the % Sm content in the alloy the decrease of  $\text{Sm}_2\text{Co}_{17}$  phase was revealed and the  $\text{Sm}_2\text{Co}_{17}$  phase was absent at all for alloy composition  $> 36.6\text{wt. \%}$ .

The present investigation reveals: (1) the same compositions and temperatures which give a high coercivity ( $H_{ci}$ ) after sintering lead to a rapid shrinkage & vice versa; (2) the rapid shrinkage was observed for the hyper-stoichiometric compositions of the  $\text{SmCo}_5$  type SPM and the remarkable increase of the volume shrinkage occurred in narrow temperature interval; (3) a model for the mechanism of shrinkage was proposed where vacancy and atom diffusion currents in the grain boundaries of different types were analyzed; (4) the influence of defect structure of the SPM takes place on atomic level and the interface atomic structure is a key for possible reversed domain nucleation on the grain surfaces, determining the magnetic properties of the SPM based on  $\text{SmCo}_5$  powder.

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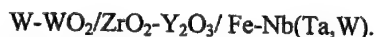


# THE THERMODYNAMIC PROPERTIES OF LIQUID ALLOYS OF SYSTEMS Fe-Nb(Ta,W), Fe-Nb(Ta,W)-Al

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Special alloys based on iron, particular multicomponents are used in difference region technique. To improve method of obtained materials, modernize legation schemes of steels, alloys and welding wires it is useful the thermodynamic properties of alloys semblance to difference steels.

For the first time activity of components were investigated with method EMF in concentration interval  $0,85 < x_{Fe} < 1,0$  at 1900 K in solid and liquid alloys of systems Fe-Nb(Ta,W) with concentration elements of the type:



The conversion of EMF this element into other with electrode compare Nb-Nb<sub>2</sub>O<sub>3</sub>, Ta-Ta<sub>2</sub>O<sub>5</sub> make throw  $\Delta G$  of formation all oxides. It was stated that alloys system Fe-W have big positive deviation from ideal solution, which become lesser on temperature rise.

The diagrams state binary system Fe-Nb(Ta) have region of equilibrium solid Nb(Ta) — liquid solution. Use coordinate of liquidus calculated activity Nb(Ta) by equations Shreder. Calculated and experimental activity Nb and Ta is well correlated between each other.

Activity Nb and Ta in liquid alloys have a negative deviation from behavior of ideal solution that correlates with type interaction of solid alloys. Our data and literature data about analogical system Fe-V(Mo) respond to one another.

To evaluate interaction energy of alloys systems Fe-W, Fe-W-Al it was studied their thermodynamical properties with calorimetry at 1900 K and calculated after Bonnier from data of binary boundary systems in Fe-Nb(Ta,W)-Al. It appears that Al introduction into iron melt leads to change in enthalpy of mixing with increase of exothermal effects alloy formation. The minimum of surfaces enthalpy of mixing all analyzed system.

All obtained data of thermodynamic properties of liquid alloys of system Fe-Nb(Ta,W), Fe-Nb(Ta,W)-Al shows on influence differences metals on activity iron and energy of solution formation semblance to steels.

# CHEMICAL BONDING OF p-,d-ELEMENTS IN $\text{Si}_2\text{N}_2\text{O}$

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Silicon nitride, oxynitride and sialon-compounds are the most extensively studied as a structural ceramic materials for the high-temperature and thermal shock resistance applications, because this materials present interesting properties, including excellent mechanical properties, good oxidation resistance and weak attack by acids up to high temperature.

In present work we report about the results of calculations of electronic structure, parameters of chemical bonding and magnitudes of solution effect of p- and d-impurities in  $\text{Si}_2\text{N}_2\text{O}$  using the diskrete variational (DV)  $X_\alpha$ -method. The parameters of calculations was tested about chemical bonds parameters of silicon nitride.  $\text{Si}_3\text{N}_4$  is a basic compound. We reseaved the covalent bonding in  $\text{Si}_3\text{N}_4$  when we didn't use the  $\text{Si}4s$ -,  $4p$ -AO and with the larger atomic distances, and ionic bond when  $\text{Si}4s$ -,  $4p$ -AO were the basic AO in MO.

We considered the  $[\text{SiM}(\text{M}')\text{ON}_6]$  clusters, where  $\text{M}=\text{Si}, \text{C}, \text{Al}, \text{Ga}, \text{Be}, \text{Mg}$  and  $\text{M}'=\text{Sr}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$  elements. We used the frozen core atomic orbitals, and didn't include the  $\text{Si}4s$ -,  $4p$ -AO in our investigation. We put the p-elements as a single defects and d-elements as not compensated, with formal valence as  $4+$ .

We can conclude that all p-atoms, except Be and Mg, have covalent bonds with oxygen and nitrogen atoms. Be-N and Mg-(O,N) bonds in contrast of other p-atoms show ionic chemical bond mostly.

The overlap population in series of p-atoms decreases and between Si-(O,N) atoms in presence of this impurity atoms increases with decrease of formal charge of p-impurity atoms from  $4+$  to  $2+$ . According to criterion Adachi about the value of overlap populations we suggest that considered p-elements will dissolve in  $\text{Si}_2\text{N}_2\text{O}$  well, except Mg atoms.

The 3d-impurities are interested because they can have a local magnetic moments and become promising systems for semiconductor device applications. We investigated the value of magnetic moments and found, that the part of this impurities are in magnetic states and other - in non-magnetic states. We estimated also a values of forbidden gap in  $\text{Si}_2\text{N}_2\text{O}$ :3d-impurities, and influence of sort of d-atoms under the chemical bonds.

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# PHASE REACTIONS IN THE TERNARY SYSTEMS $\text{HfO}_2(\text{ZrO}_2)\text{-Y}_2\text{O}_3\text{-La}_2\text{O}_3$ AT HIGH TEMPERATURES

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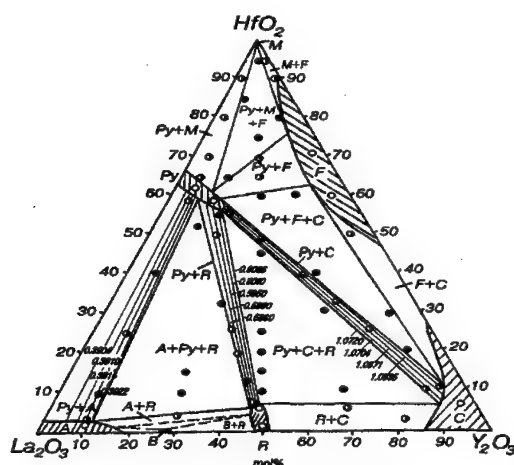
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Zirconia(Hafnia)-based materials are used in high-temperature electrolytes of fuel-cells and sensors. For the fuel cells application the main problems are concentrating in the search of the best ion conductors by addition of complex dopants and grain boundary interface area increase. Such phases like stabilized zirconia and yttria doped  $\text{La}_2\text{Zr}_2\text{O}_7$  are formed in the system  $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-La}_2\text{O}_3$  and can be interesting candidates for the oxide ion conductor in fuel cells. However, phase equilibria in the mentioned ternary systems were not studied in details.

Phase equilibria in the systems  $\text{HfO}_2\text{-Y}_2\text{O}_3\text{-La}_2\text{O}_3$  and  $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-La}_2\text{O}_3$  were studied in the temperature range 1250 - 2500 °C by both

experimental methods and development of a mathematical model for the liquidus surfaces by means of reduced polynomial methods. Isothermal sections at 1250, 1600, 1900 °C were developed for the  $\text{HfO}_2\text{-Y}_2\text{O}_3\text{-La}_2\text{O}_3$  and  $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-La}_2\text{O}_3$  systems. The similarity of the phase diagrams was displayed in the structure of the liquidus and solidus surfaces and isothermal sections. Solid solutions are based on the initial oxides (T- and F-



Isothermal section at 1250 °C

zirconia, M-, T- and F-hafnia, A-, B and H- lanthana, C- and H- yttria) and the intermediate compounds  $\text{La}_2\text{Zr}_2\text{O}_7$  (Py),  $\text{La}_2\text{Hf}_2\text{O}_7$  (Py),  $\text{LaYO}_3$  (R).

The research described in this abstract was made possible in part by Grant 0213-95 from the INTAS-Ukraine.

MODELING OF PROCESSES  
PASSING ON FRONTIER SOLID OXIDE – LIQUID PHASE

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Welding, soldering, tinning, synthesizing substances from melts are important technological processes passing on frontier division of phases solid – liquid. Quality of compounds, seams and covers forming depend on type interaction in zone of contact. That is way necessary modeling this processes with aim to prediction of type interaction, chose of optimal composition contacting phases, provide high quantity of formation.

At the contact of non-metal, oxide materials with liquid alloys. The reaction proceeds forming different oxide phase, in some cases with known composition. For such complicated systems the change of Gibbs energy of surface reaction was calculated.

Oxides of Al and Si at high temperatures dissociate forming metal and oxygen atoms dissolving in liquid alloys.

For example have been analyzed means  $\Delta G$  of reactions at 1400 K, passing with mole fraction of titan 0,1, in witch can form oxygen, liquid solution of oxygen in alloy ([O]) or oxide phases ( $TiO$ ,  $Ti_2O_3$ ).

Values of  $\Delta G$  are greatly smaller zero at forming liquid solution of oxygen in titan connection alloys. The process of interaction don't finish on this stadium and pass deeper to formation  $TiO$  at  $\Delta G \approx -400$  kJ. It is conditional that much energy calorification used to heating system and lead to passing reaction with deeper oxidation of titan. If  $\Delta G(TiO) \ll \Delta G(Ti_2O_3)$  process of oxidation finish with formation oxide more high degree oxidation of titan ( $Ti_2O_3$ ). On other hand, if  $\Delta G(TiO) \approx \Delta G(Ti_2O_3)$  the reaction is fishing at formation stadium  $TiO$ .

Thus, to predict and regulation of product of interaction on frontier division  $Al_2O_3$ -(binary liquid alloy) necessary calculate and compare values of  $\Delta G$  at different stadium of reaction between.

# CALCULATION OF THERMODYNAMIC PROPERTIES OF ALLOYS WITH USED DIAGRAMS STATE BINARY AND TERNARY SYSTEM

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The thermodynamic properties of alloys binary and ternary system have important means for determination optimal conditions realization of some technological processes: alloying, welding, deoxidation, desulfuration, soldering, tinning of details. But because of aggressive, heigh melting and heigh boiling of components investigated not always succeed.

The thermodynamics properties of alloys and them the diagram state are very connect. The diagrams states of many binary and some ternary system well-known, therefore can used them for forecast of the Thermodynamic Properties of Alloys, if one or both components are aggressive or difficult melt. For region of diagram state which characterize with equilibrium liquid solution-solid component the best is equation:

$$\mu_1^l = \mu_1^s; \mu_1^l + RT_p \ln a_1 = \mu_1^s; RT_p \ln a_1 = \mu_1^s - \mu_1^l; \Delta \bar{G}_1^{nada} = -\Delta \bar{G}_n - RT \ln x_1$$

Calculated activity components from this correlation agreement with experiment.

From the diagrams states which have regions of equilibrium liquid solution - solid component (solid solution) we elaborated the methods witch allow of calculation the thermodynamics properties of alloys binary and ternary system with satisfactory precision, used coordinate of liquidus corresponding heat melt of components and in some cases thermochemical parameters solid and liquid phases.

For regions of diagram state with congruent melted compounds more efficient is improvement method of Hauffe-Wagner with the help to calculate activity of components in liquid alloys.

For the first time activities of components binary system Si(Ge, Al, Ni)-metall and Fe(Ni,Cu)-Nb have been predicted in wide interval of composition. For this we used one or two fragments of diagram state.

We calculated of silicon in liquid alloys ternary system from the diagrams Cu - Si - Al. Find out that obtained means activity of silicon well correlire with calculated on equation Bonnier on base activity of silicon in binary boundary system Si - Cu(Al).

**SEMINAR C.**  
**ADHESION AND INTERCONNECTION. COATINGS 76-109**

# FORMATION OF BRAZED JOINT OF $\text{Si}_3\text{N}_4$ CERAMICS - METAL WITH USE OF CERAMIC INTERLAYERS WITH VARIOUS THERMOEXPANSION

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The main problems in formation of brazed ceramics - metal joint parts, in particular for the  $\text{Si}_3\text{N}_4$  wheels of turbine with the steel shaft, are distinctions of thermal expansion ( $\Delta\alpha$ ) of materials, and also an absence of reliable technology of the brazing as well as design of brazed joint.

The mismatch  $\Delta\alpha$  for these materials vapour reaches  $6...12 \cdot 10^{-6} \text{ grad}^{-1}$  that results in high thermal stresses and a hazard of ceramics fracture. In this research a design of brazed joint is considered in which the  $\text{Si}_3\text{N}_4$  - TiN ceramics inserts as 4-6 pieces are placed between  $\text{Si}_3\text{N}_4$  and the metal, the incerts above having various  $\alpha$  ( $\alpha_n - \alpha_{n+1} = 1..2 \cdot 10^{-6} \text{ grad}^{-1}$ ).

The alloy Cu-Ga-Ti system is used as a solder. The thickness of soldered junctions was less than  $25 \mu\text{m}$ . At such thickness of junctions the bending strength of brazed joint reaches  $0.95 \sigma_{\text{bend.}}$  of monolithic ceramics; with an increase of metal interlayers thickness the strength of joint diminishes. Hereby in the zones of ceramics near metal interlayers an increase of length of cracks under the hardness indents is found as well.

With an use of the finite elements method the analysis of thermal stresses in a material is carried out. Near to a surface an extremely non-uniform stress distribution with considerable tension in the zones with thickness about  $50 \mu\text{m}$  near the ceramics - metal boundary is found. It is shown, that an embrittlement of ceramics and a decrease of brazed joints strength is conditioned by the edge effect of thermal stresses redistribution.

## CERMET COMPOSITES ON THE<sup>77</sup>BASE OF TITANIUM POWDERS

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The progress in the modern machine-building is mainly defined by the development and application of new materials, in particular ceramic and cermet materials, and products made from them. These materials can be used for laminated structures, products of an intricate shape and other products with special properties.

However, to manufacture cermet components and units, which combine the elements of ceramics and metal, it is necessary to use different methods of their joining. Such methods as brazing, adhesive bonding, diffusion bonding, etc. are used as main methods.

The use of the diffusion bonding for a direct joining of ceramics with metal, in particular titanium, is not yet a solved problem. The well-known technologies of diffusion bonding of these materials are based on using soft interlayers. This significantly complicates the technology of the process, not guaranteeing the required properties, and permits solution of only some separate problems.

In addition, to provide the required geometric shape is a complicated problem of the existing methods of manufacture of cermet components and units, because it is often difficult and sometimes impossible to machine the cermet elements of the components with a preset accuracy.

The offered technological process of diffusion bonding consists of joining the monolithic titanium with a porous metal prefabrication made from titanium powder, i.e. homogeneous metal.

After bonding these prefabrications can be easily subjected to the mechanical treatment for producing the required shape with a necessary accuracy. Then the ready components are subjected to heat treatment in an activated gas medium to impart the ceramic properties to them. Taking into account that the interaction of porous bodies with an active medium proceeds more intensively than that of monolithic bodies, the porous part acquires properties which are close to ceramics, while the monolithic part of the prefabrication preserves its physical and mechanical characteristics.

Titanium was used as a base material for investigations, while nitrogen was used as an active gaseous medium.



## THIN-FILM AND DISPERSION COMPOSITION MATERIAL

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In work considered algorithm of goal-directed getting composition material including: choice of target characteristics, forecasting, directed syntheses, qualification, technology and ensuring making the able to meet competition products with the new quality and increased reliability methods under low temperatures.

Characteristics of thin-film and dispersion compositions including join with nitrogen, asked and complex oxides hang from the composition, warm-up and other conditions of syntheses, as well as textures of forming phases, as evidenced by installed correlation by dependencies: condition of syntheses - a composition - a structure - a degree dispersion - a characteristic.

Developing models of laminated compositions taking target features into account, nature composition component, physical and chemical compatibility, have allowed to choose optimum compositions, structures and for the first time get a thin-film metal-not metal covering AlN-Ag-AlN, AlN-Cu-AlN, AlN-Cu(Be,Mg)-AlN, TiO<sub>2</sub>-Ag-TiO<sub>2</sub>, TiO<sub>2</sub>-Cu-TiO<sub>2</sub>, TiO<sub>2</sub>-Au-TiO<sub>2</sub>, ZrO<sub>2</sub>-Ag-ZrO<sub>2</sub>, CeO<sub>2</sub>-Ag-CeO<sub>2</sub>, HfO<sub>2</sub>-Ag-HfO<sub>2</sub>, CeO<sub>2</sub> (Ce<sub>2</sub>O<sub>3</sub>)-Ag-CeO<sub>2</sub>(Ce<sub>2</sub>O<sub>3</sub>) with increased thermo photo by energy stability.

From film forming dissolve are formed dispersion composition systems with developed silicate by the framework and portioned in him metallic constituting of PDP aluminum. Dispersion to compositions metallic zirconium with its oxides and join with nitrogen Zr-ZrN; Zr-ZrON; Zr-ZrN-ZrO<sub>2</sub> received as a result cryogenic processing. Offered and motivated with a develop framework and firmly electrolyte models gas an absorption tinned compositions.

Regularities of manifestation composition compatibility and reactionary ability of thin-film and dispersion forming their not balance of conditions stipulated by specifics of, caused by conditions of syntheses, physical compatibility with the substrate material, springy voltages, promoting phase, structured and chemical conversions. Processes of association and phase transition are chemical stability accompanied by the loss of, but structured realignments bring about arising the borders between grain that also reduces chemical system stability.

## High Strength High Temperature Brazed and Diffusion Bonded Metal/Silicon Nitride Units

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The brazed silicon nitride/metal joints for long duration working in conditions of torsion loading at high temperature in air medium were elaborated. Two technological processes for joints fabrication are proposed: 1) active brazing through plastic metal gasket or special high deformable metal wire; 2) diffusion bonding with use of plastic (aluminium) gaskets. Designs of the joints including combined adhesion and mechanical bonding were considered. Brazed and diffusion bonded titanium/silicon nitride and stainless steel/silicon nitride cylindrical units were manufactured. The samples produced 100 cycles of loading on regime as follows: loading by a torsion stress of 50 MPa at temperature 600 °C on air medium, endurance under this load during 1 hour, cooling to room temperature. The maximum torsion strength value for silicon nitride/metal joints at 600 °C in oxygen containing medium was 120 MPa.

## CAPILLARITY PHENOMENA IN THE TiC / (Cu, Al) SYSTEM

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Titanium carbide has a high melting point, displays extremely high hardness and shock resistance and its electrical conductivity is comparable to that of metals. These properties make it a promising candidate material for some electrical applications. In particular, the titanium carbide-copper system is a metal-ceramic composite that provides a favorable combination of electrical and mechanical properties.

The interfacial properties of metal-ceramic systems, and, in particular, the wetting behavior, play an important role in the evolution of the microstructure during the processing stages of metal-ceramic composites. The microstructure is a determining factor of the mechanical and physical properties of these materials.

The wetting behavior in the TiC/(Cu, Al) system has been studied by the sessile drop method over the entire Cu-Al alloy concentration range at 1050°C. The experimental results show that the presence of oxygen contamination on the TiC surface plays a major role in the capillarity phenomena. Molten Cu impregnates unsintered preforms and the sintered substrates made from TiC powders with low oxygen contamination on the surface as long as their porosity was higher than 10 vol%, without spreading on the surface. Impregnation started after 2-3 min (incubation period) and was completed within ~1 min. The contact angle between the molten Cu-Al alloys and the TiC substrates of low oxygen content decreases sharply for alloys with a higher than 15 wt.% Al. Surprisingly, for the substrate with high oxygen contamination even at small Al content of <3 wt.% a very significant decrease of the equilibrium contact angle to 20° was observed.

According to the experimental results and the thermodynamic predictions, the wetting kinetics in the presence of pure Cu are controlled by partial dissolution of the titanium carbide phase. The presence of oxygen contamination on the ceramic surface strongly inhibits this reaction. The wetting behavior in the TiC-(Cu, Al) system is controlled by reduction of the oxidized layer on the ceramic substrate surface. In-situ deoxidization of the Cu-Al liquid drop and of the surface of the TiC substrate by evaporation of aluminum oxide may also contribute to the wetting process.

The results that were obtained in this study can be used for producing TiC-Cu or TiC-(Cu, Al) infiltrated composites for structural and electrical applications.

**MICROSCOPICAL THEORY OF THE BIMETALLIC INTERFACE THERMODYNAMIC PROPERTIES: 1. ADHESION ENERGY OF THE TWO METALS**

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On the basis of the manyparticle self-consistent approach in theory of the inhomogeneous metal systems the free energy of the bimetallic system with planar interface in any order of the perturbation theory on the electron-ion pseudopotential is obtained. In second order of the perturbation theory the energy of the bimetallic system is calculated. The pair interactions and correlations in bimetallic system taking into account. The adhesion energy of the two contacting metals in arbitrary phase state (solid, liquid, amorphous) is obtained. The adhesion energy expressed in terms of the metal-vacuum surface energy for each contacting metal and "interfacial energy" of the bimetallic system. The metal-vacuum surface energy and "interfacial energy" in terms of the interparticle interaction potentials and partial ion distribution functions are expressed. The model calculation of the adhesion energy for miscible and immiscible pair of liquid metals (Na-K, Na-Al, Na-Zn, Cs-Li) are executed. Numerical calculations of the adhesion energy have been indicated the principal role of the second order terms of the perturbation theory. The adhesion energy of the two liquid metals is nonsensitive thermodynamic function to stratification effect.

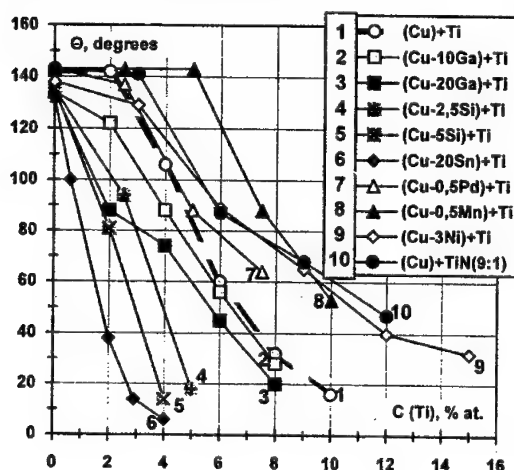
# **TITANIUM SOLVENT SECOND COMPONENT INFLUENCE ON SILICON NITRIDE CERAMIC WETTING BY MELTS BASED ON Cu-Ti**

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The causes of metal melts spreading on non-metal materials are not established for certain to nowadays. Theirs are explained either by the intensity of reactions at the interface which is determined by Gibbs energy changing for the interaction or the processes which are not related with mass transfer through interaction surface (with the reaction products properties or adsorption). In the first case the wetting depends on the activity value of an capillary-active doping (e.g. Ti) at the first stage of the interaction process, and in the second one the wetting is defined by the activity equilibrium (pseudo-equilibrium) value. The difference is caused by appearing of the wetted substrate elements (the reaction products) in the metal solution.

The influence of some metals (Mn, Pd, Ni, Ga, Sn, Si) doped in the Cu-Ti melts on  $\text{Si}_3\text{N}_4$  wetting at  $1150^\circ\text{C}$  in vacuum  $10^{-3}$  Pa are investigated in the study (Fig.). Used dopings permit to change Ti activity in the solution and contact interaction intensity. The doping of metals in Cu-Ti melt which decrease contact reaction intensity at constant titanium concentration result in intensifying of capillary characteristics as follows from fig. Present conclusion confirms the adsorption wetting mechanism of non-metals by metallic solutions.



The results of the interaction area profilographic and microstructure investigations are presented, too.

Fig. The influence of metal dopings in Cu-Ti melts on  $\text{Si}_3\text{N}_4$  wetting at the temperature  $1150^\circ\text{C}$ .

# GAS-THERMAL CHROMIUM-BASED COATINGS — AN ALTERNATIVE TO GALVANIC CHROMIZING

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The high functionality of chromium galvanic coatings has predetermined their broad use in various industries. The process is ecologically harmful, that sets the tasks of its replacement. The use of gas-thermal coating from chromium-based alloys is one from alternative paths of the task fulfillment.

The possibility of replacing the expensive and ecologically harmful technology of chrome electroplating by the process of gas-thermal spray deposition of high-temperature, wear-resistant chromium-based coatings is demonstrated in the work. Properties of chromium-based spray coatings obtained by the methods of gas-thermal spraying, of electroplating, ordinary and supersonic gas plasmas, detonations and galvanic have been analyzed.

It is shown, that using various spraying processes it is possible to obtain coatings with various hardness, porosity and adhesion strength characteristics (Table).

**Table. Influence of technical characteristics on properties of chromium-based gas-thermal coatings.**

Method	Kind of material, its size in mm	Common porosity, %	Cohesive strength, MPa	Microhardness, ITIa
Gas-thermal	Wire, 3000	6-18	16-25	3,2-5,2
Electric arc bonding	Wire, 3000	4-2	20-25	3,5-5,5
Plasma	Powder, 40-60	3-6	21-32	5,0-7,0
Supersonic plasma				
air-gas	Powder, 40-60	1-3	40-50	7,5-10,0
Detonation	Powder, 40-60	0,5-1,5	45-60	8,0-10,5
Galvanic	Electrolyte	0,03	50-60	7,5-10,0

The surface structure and phase composition of chromium-based coatings have been studied using X-ray diffractometry and electron microscopy. Their characteristics in conditions of friction, high temperatures and electrochemical corrosion have been defined.

Operation conditions and economic expediency of gas-thermal coatings from chrome-based alloys dictate the choice of spraying method.

OBTAINING OF ANTICORROSIVE COATINGS WITH THE USE OF  
PRETREATED ZINC POWDER

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The traditionally used powder media for dry galvanizing are toxic, sintering-prone, do not present stable reuse outcomes. The application of dry galvanizing in a zinc powder media, that underwent hydrothermal preliminary treatment (HTT), preventing sintering of powders at high temperatures, allows to step up the process and to eliminate the above said disadvantages.

Within the framework of this study, experimental research of the process of diffusion saturation in HTT mixtures was conducted. Processing of zinc powder of a brand ПЛ-4 was carried out in distilled water boiling in the open container. Dry galvanizing under temperatures 450°C up to 600°C during 1 and 3 hours. The mixture consisted of 100% HTT zinc powder. Samples of 15 brands of structural steel were used. Investigation into effect of temperature of the CTT (chemical-thermal treatment) process and steel composition on thickness and structure of the obtained coating revealed linear dependence between CTT temperature and layer thickness. The base coating represents  $\delta$ -phase. The structure of diffusion zinc coating obtained in HTT mixtures, contains:  $\alpha$  (solid zinc solution in  $\alpha$ -Fe) on the saturated articles surface and G-phase. With the increase in CTT holding time, the layer thickness rises. Visual inspection showed, after CTT the samples had a smooth, light gray surface without traces of sticking of mixture.

Thus, the use of HTT powder media allows to receive high-quality diffusion coatings in the given conditions.

# EVALUATION OF INFLUENCE OF RESIDUAL THERMAL STRESS ON FRACTURE TOUGHNESS OF BRITTLE COATINGS

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In conditions of local contact loading by tough Vickers indenter strong influence of an initial field of residual thermal stresses  $\sigma^r$  on a failure resistance of brittle coatings has been discovered. That is why in connection with revealed effect of elastic  $\sigma^r$  on the geometry of the crack path in the vicinity of the indenter impression overall fracture toughness of coatings is offered to evaluate as a total combination of the  $K_{Ic}(y, \varphi)$  values calculated from the extent of cracks occurred on the distance  $y$  from the surface and directed orthogonally to operating  $\sigma^r$  ( $\varphi = 0, \pi/2$ ) [1].

According to proved linear dependence of fracture toughness as a function of  $\sigma^r$  the  $K_{Ic}(y, \pi/2)$  criterion is changing on the value of stress intensity factor at the top of metastable submicrocrack with extent  $C_c$  that is affected by residual stresses  $\sigma^r$  acting normally in its vicinities. The  $K_{Ic}(y, \pi/2)$  values are increasing under compression stress and decreasing under tensile stress. In condition where  $d \gg D$  (where  $d$  is impression diagonal and  $D$  is linear grain size) that is observed while equaxed fine grained layers (typically for layers made of carbides, nitrides, and silicides, etc.) being tested the function  $K_{Ic}(y, \pi/2)$  from  $\sigma^r$  is considered to be given in form (due to additive properties of elastic stresses) as follows:

$$K_{Ic}(y, \pi/2) = K_{Ic}(y, 0) - \bar{\sigma}^r \sqrt{C_c},$$

where in accordance with experimental data  $C_c$  could be accepted as a half of linear grain size that is estimated to be  $\sim 10^{-6}$  m.

On examples of boride coatings ( $FeB$ ,  $Fe_2B$ ) it has been shown that in particular case of coarse grained layers ( $d \ll D$ ) absence of sensibility of experimentally registered  $K_{Ic}(y, \pi/2)$  values from  $\sigma^r$  is caused by small linear size of  $C_c$  that is determined for the case as well as for the case of monocrystals by length of the activated zone in dislocation slip line and does not exceed  $\sim 10^{-10}$  m.

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**PHISICOCHEMICAL PECULIARITIES OF ADHESION OF THE  
YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7.5</sub> COATINGS FABRICATED BY THE GAS DYNAMIC  
DEPOSITION TECHNIQUE**

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For practical application of high temperature superconducting (NTSC) coatings it is highly essential to elucidate the causes for reliable strong binding (adhesion) of the coating to the substrate material. To date this problem is almost not studied.

Using the gas dynamic technique [1] NTSC YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7.5</sub> coatings of 3 μm thick have been fabricated on the SrTiO<sub>3</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, BeO, Cu and Ag substrates. The optimal heat treatment regimes and the temperatures of transition to superconducting state were determined. The value of adhesion of the coatings to the substrates made of various materials were qualitatively examined by the microindentation technique using the value of coating chipping. It is established that the adhesion depending on the substrate material reduces in the series SrTiO<sub>3</sub>(single crystal (100)) → MgO(polycrystal) → MgO(single crystal (100)) → Ag → Cu/Cu<sub>2</sub>O → BeO(polycrystal) → Al<sub>2</sub>O<sub>3</sub>(polycor) → Al<sub>2</sub>O<sub>3</sub>(sapphire) → ZrO<sub>2</sub>(single crystal(100)). The copper substrate was previously coated with a Cu<sub>2</sub>O buffer layer irradiated by Co<sup>60</sup> γ-rays [2]. A correlation was observed between the value of adhesion and the degree of agreement of the crystal lattice parameters of the coating and the substrate. There was also found a correlation between the value of adhesion and that of the energy of breaking the chemical bond of metal atoms with oxygen atoms in the substrate material: the lower the energy, the stronger the adhesion. This correlation is specified by the technological peculiarities of fabrication of coatings by the gas dynamic technology, where the activation factors are the contact heat exchange between the powder particles and the substrate as well as the contact elastic-plastic deformation.

1. V.A.Varavin, E.M.Gololobov et al. Pis'ma v ZhTF, 1993, v.19, No.16, p.51-58
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## WELDING OF DISPERSION-STRENGTHENED COMPOSITES WITH AN ALUMINIUM MATRIX

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In many of the present-day industries such requirements to the structural materials as low weight, high strength and rigidity, good resistance to fatigue loads and wear, are the determinant ones. Composites which are known to combine the properties of two or several metallic or non-metallic materials, meet such requirements in the most complete manner. However, the potential capabilities for the composites use in structures for various applications are restrained by the absence of reliable processes of their welding. Under the conditions of direct action of a high-temperature heat source (arc, plasma, electron or laser beam) on the strengthening particles, they decompose with the subsequent interaction of the components both with the matrix material and with hydrogen evolving from the base metal in this case. These processes prevent the formation of sound welded joints.

The work gives a comparative evaluation of the processes of welding Al-matrix composites strengthened by disperse particles of SiC and  $Al_2O_3$  with and without melting-off of the edges being welded.

The main process parameters are established, as well as the factors providing the production of high-quality joints of composite materials without edges melting-off, through a filler layer deposition by dispersion. In the case when aluminium alloys are used as the filler material, whose maximal strengthening is achieved as a result of natural ageing, the properties of the joints reach the level of the matrix alloys properties.

The practical implementation of the process was performed in an electron beam unit with local surface melting of a quickly rotating cylindrical billet by an electron beam and a fine-drop transfer of the filler onto the appropriately prepared surface of the edges being welded. Optimization of the parameters of this process, conditions of its implementation, selection of the most rational forms of edges preparation and filler material grade, will allow a broader use of composite material in welded structures, and development of not only new designs, but also of unique products.

FEATURES OF THE STRUCTURE AND OF WELDING OF A  
NANOCOMPOSITE OF AL-AL<sub>2</sub>O<sub>3</sub> SYSTEM PRODUCED BY  
CONDENSATION UNDER VACUUM

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Studied are the microstructure and weldability by fusion welding of a finely-dispersed composite material of Al-Al<sub>2</sub>O<sub>3</sub> system, produced by deposition of aluminium and aluminium oxide from the vapour phase under vacuum. Such a method was used to manufacture a sheet material (condensate) of 0.5 to 0.8 mm thickness with 1.6 to 3% content of aluminium oxide.

The initial microstructure of the condensate is characterized by up to 0.2 mm long crystallites oriented normal to the surface. Disperse inclusions of oxides are located mainly along the crystallite boundaries. Investigation of the fine structure by the electron microscopy methods revealed blocks with an ordered polygonal structure characteristic of cast metal. Oxide inclusions of 10 to 50 nm size are distributed in a relatively uniform fashion. The particles spacing is 60 to 100 nm. The base metal microhardness depends on the oxide content and is 600 to 700 n/mm<sup>2</sup>.

The features of the joints formation were studied when microplasma welding in MPU-4 unit was used. It was established that the nature of the condensate melting and solidification in welding is essentially different from that of the series-produced aluminium alloys.

When butt joints are made without the filler, each edge is melted off separately and no common pool is formed. For welding with a filler from one and both sides without a gap in the butt, an absence of the edges joining and development of defects in the form of oxide films and discontinuities is also typical.

A sound formation of the joints was achieved in welding of butts with up to 1 mm gap and beads deposition from two sides. The joint formation under these conditions occurs by the type of braze-welding and the weld is mainly formed from the filler metal. A feature of the macrostructure of the metal of such welds is its higher dispersity than in welding of the series-produced alloys, this being related to the availability of the ready crystallization sites in the form of disperse oxide particles.

Mechanical tests of welded joints with the use of SvAMg6 filler, demonstrated that their ultimate strength is on the level of the base metal and is equal to 136 MPa.

### THE NEW BRONZE-FLUOROPLAST COATINGS

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The exploitation conditions of modern equipment in gaseous and liquid mediums, in dropped temperature and cosmic vacuum also are often excepting the possibilities of application of traditional liquid lubricants. That is why the antifriction characteristics of friction centers can be improved by the addition in materials of the solid lubricants as molybdenum disulfide, tungsten diselenide, calcium difluoride, and fluoroplast.

We studied the possibility to use the ultradisperse polytetrafluorethylene (UPTFE) by production of dusting coatings for attaching them of antifriction properties. The production of UPTFE is based on thermogaseousdynamic processing of various forms of fluoroplast-4 including their waste materials. The UPTFE particles obtaining by thermogaseousdynamic method are regular spherical form with the spherulite structure. The UPTFE dust is monofractional with the particles from  $1.0 \mu$  to  $0.1 \mu$ . The surface of spherical ones activated by carbonyl groups is improved of adhesion of particles to metallic machine details.

The plasma dusting of the same powder bronzes in plasmatron with argon as plasma gas obtained the flame-sprayed porous coatings on the metal bronzes. The pores packing of dusting coatings was carried out by the fluoroplast suspension with fluoroplast-4, UPTFE and n-buthylalcohol in hermetically sealed container in vacuum. The best result was obtained with using of UPTFE suspension from waste fluoroplast-4 with  $(0.4 \pm 0.3) \mu$  spherical particles. The best pores packing in the thickness of coatings that was confirmed by the XPS method may interpret this fact. The tribotechnical tests of coatings for disk-disk friction couples with the chilled steel as a contrbody showed that the friction coefficients are equal 0.12-0.10 when pV is 6 m/s and pressure is 0.9-6.0 MPa. It was established that the combined coatings can be successfully operated without liquid lubricants in aqueous (in sea water also), in air, in noble gases mediums and in vacuum and can be recommended for production of friction details of different pumps and cryogenic and cosmic apparatus.

### INFLUENCE OF AGING ON THE ADHESIVE STRENGTH OF THE GLUE COMPOSITIONS

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Epoxiurethane glue compositions which are characterized by high adhesion to substrates of various surface energy was developed on the base of polyfunctional oligomers with altered flexible and rigid blocks of the chain.

Compounds of amine and anhydride types: diethylenetriamine (DETA) and isomethyltetrahydrophthalic anhydride (IMTHPHA) were used as hardeners.

Influence of aging on the adhesive strength of glue joining of the metal surfaces was investigated. Influence of high temperatures and aggressive environments (acids, alkalizes and boiling water) on the adhesion parameters of the hardened epoxiurethane compositions was considered as aging factors by means of ATIR-spectroscopy.

It was shown that glue compositions hardened by IMTHPHA are more thermally and hydrolytically stable due to peculiarities of its structure formed in the presence of this hardener. Performed experiments allow to recommend perspective glue compositions (adhesives) for the present-day techniques. Certain of the developed and investigated glue compositions were successfully tested for application in radio engineering, medical technique, and space technique (producing solar batteries cells for space ships).

## DEVELOPMENT AND STUDY OF PROPERTIES OF COMPOSITE CATALYSTS BASED ON METALLIC NETTED FRAME

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Ceramic-based catalysts have low heat conductivity leading to their local superheating that causes a non-stability of their catalytic activity. Metal-based catalysts have this disadvantage significantly reduced.

The report describes data on the development and investigation of properties of 3-dimensional netted structure-based catalysts made of metallic fibers. Such structures have good gas dynamic properties, a greater specific surface that can be adjusted during their formation process. A 3-D metal frame is covered with a pyroceramic adsorption film deposited by the electrophoresis method with subsequent coverage with a catalytically active film (Pd, Pt, Ph, etc) by infiltration and thermal treatment techniques.

The effect of heat treatment temperature and thermal cycling on the value of the metal-pyroceram adhesion was determined. The influence of the sintering temperature of the 3-D metal fiber frame-deposited pyroceram film on the specific surface of the pyroceram film, its adsorption ability and humidity absorption, was estimated.

It was shown that the catalyst containing 0.4 wt% of palladium on a metallic netted carrier with a pyroceram film, has a 100 % activity in the oxidation reaction of carbon monoxide already at 165 °C.

Said catalyst was tested having the porosity of the metallic frame of up to 90 % during the conversion of carbon monoxide with water vapour at 200, 33 and 400 °C. Chemical reactions were examined that occur upon the catalyst surface and chemical process parameters were studied.

The research results can be used in the design of high performance catalysts for industrial and environmental protection application.

# THE THERMODYNAMIC PROPERTIES OF SOLID AND LIQUID ALLOYS OF SYSTEM FE-CR AND FE-CR-M

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Stainless steels and special alloys based on iron are used in cryogenic and chemical apparatus. At welding of the details from this materials appear shot and cold breaks. To modernize legation schemes of steels, alloys and welding wires it is useful the thermodynamic properties of alloys semblaut to stainless steel.

Activity of components were investigated with method EMF in temperature interval 380 - 953 K and at 1900 K in solid and liquid alloys of systems Fe -Cr and Fe -Cr -M with concentration chain of the type:

Cr/CrCl<sub>2</sub>(Cr<sub>2</sub>O<sub>3</sub>)- glycerin (KCl-LiCl or CaO-SiO<sub>2</sub>)/[Cr].

It was stated that alloys system Fe - Cr have positive deviation from ideal solution, which become lesser on temperature rise. Introduction of nickel into ironchromium alloys with 18 %-21 % Cr gives a drop in chromium activity.

Activity Cr in liquid alloys have a little negative deviation from behavior of ideal solution that correlates with data of solid alloys. Our data and literature data respond to one another.

We studied influence of some elements on activity of chromium in liquid alloys of system Fe -Cr -M and calculated interaction parameters  $e_{Cr}^M$ . It appears that  $e_{Cr}^M$  are positive for wolfram, molibdenium and negative for nickel, titan, aluminium. Thus changing of composition of system Fe-Cr-M one way change, chromium activity (and other elements) monitoring properties of initial Fe-Cr alloys.

To evaluate interaction energy of alloys semblance to stainless steel it was studied their thermodynamical properties with calorimetry at 1960 K and calculated after Bonnier from data of binary boundary systems. It appears that Ni introduction into ironchromium melt leads to negligible change in enthalpy of mixing with decrease of exothermal effects alloy formation.

All obtained data of thermodynamic properties of solid and liquid alloys of system Fe-Cr and Fe-Cr-M shows on influence differences metals on activity chromium and energy of solution formation semblance to stainless steels.

# WETTING AND CONTACT INTERACTIONS IN THE $\text{TiC}_x/\text{Al-Ni}$ SYSTEMS

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The effect of  $\text{TiC}_x$  composition ( $x = 0.7 - 1$ ) on its wettability by molten Al-Ni alloys was examined by the sessile drop method vs. Ni concentration, time of contact and temperature. Compared to pure Al, small amounts of Ni (up to ~5%) improve the wetting in most cases. Further increase of the Ni content leads to higher wetting angles. The wettability of  $\text{TiC}_x$  by Al-Ni (up to 30%Ni) alloys is enhanced with decreasing carbone content. Studies of the  $\text{TiC}_x$ /alloy interfacial region by SEM/EPMA show the formation of new intermetallic phases in the  $\text{TiC}_x/\text{Al-Ni}$  systems that are expected to affect the mechanical properties of the metal/ceramic composite material.



# ENGINEERING STRENGTH AND ELASTIC-PLASTIC PROPERTIES OF COATINGS MADE OF TITANIUM NITRIDE

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With the help of novel methods [1,2] of micromechanical tests of materials by means of local contact loading by tough Vickers indenter the complex of mechanical properties including elastic deformation  $\epsilon_e$ , plasticity parameter  $\delta_H$ , and also fracture toughness  $K_{Ic}$  have been determined for coatings based on titanium nitride. Values of the mechanical parameters above were determined under test conditions that ensure correct comparison with elastic-plastic contact. Evaluation of mechanical parameters of coating are given while their content on nitrogen is varied in the interval of  $32 \text{ at.\%} \leq N \leq 44 \text{ at.\%}$  and also with modification of texture rate of phase  $\delta$  - TiN in the directions such as [100] and [111].

It is revealed that parameter  $\delta_H$  is linearly increasing with increasing of nitrogen content in coating while  $\epsilon_e$  and HV are decreasing. In full accordance with existing views about strength and plasticity of brittle materials it is shown that contrary to typically metallic layers for which HV и  $K_{Ic}$  are changing on contrary directions with variation of content and structure coatings made of titanium nitride are characterized in the general case by absence of correlation between  $\delta_H$  parameter and  $K_{Ic}$  criterion. Moreover, in accordance with results of comparative analysis nitrogen content in coating exerts preferential influence on plasticity characteristic ( $\delta_H$ ) and crystallographic texture determines preferably resistance to fracture ( $K_{Ic}$ ). This leads to the fact that under comparable values of plasticity parameter  $\delta_H$  fracture toughness  $K_{Ic}$  for coatings of the same phase content ( $\delta$  - TiN) can differ for 30% and more.

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# THE ADHESION, MICROHARDNESS AND MICROSTRUCTURE OF A CHROMIUM DEPOSITS, OBTAINED FROM A FLUORINE-CONTAINING ELECTROLYTES.

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It is established essential difference of the chromium electrodepositions from electrolytes with various ligands: F (I) and  $\text{SO}_4^{2-}$  (II). The chromium coatings were deposited on a steel substrate in wide range (293-363 K). These coatings (I) had a microcrystalline morphology of surfaces, higher microhardness (on Vickers) and a high adhesion to substrate [1]. This is evidence of a best wearproofability for details with such coatings. The formation of a large-crystal texture of coatings with good adhesion to substrate takes place in the temperature range 343-363 K. The crystallite sizes for coating (I) is  $10^{-3}$  cm and  $10^{-7}$  cm for (II).

The fluorine-containing electrolytes  $\text{NbF}_6^{2-}$ ,  $\text{TiF}_6^{2-}$  give rise to high microhardness of deposits, due to chemical nonuniformity and by the defects of chemical nature after type the Charge Transfer Complexes of d-metals (CTC-eng., KPZ-rus; they had much a growth dislocations, formed at them [2]). These conclusions are confirmed by different methods of investigations of the crystalline (X-ray) and of the electronic structures (XPS). It was established essential decreasing of the crystalline lattice for chromium (I) in comparison with one for chromium (II):  $a=0.27057$  and  $a=0.28839$  nm, respectively [1]. The microhardness of this coatings are: 4.29 and 1.4 gPa, respectively. Other peculiarities and advantages of the chromium coatings, obtained from fluorine-containing electrolytes, are discussed too.

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### **Improvement of Adhesion of the Organo-Inorganic Layered Composite Materials Due to Incorporation of Polymeric Metallophosphates**

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Polytetrafluoroethylene (PTFE, Teflon) has got a complex of valuable properties, such as high chemical and thermal stability, low friction coefficient, nontoxicity and very low adhesion to the majority of materials. The problem which appears is how to provide sufficient adhesion of the PTFE coating to the support materials. Often it is also important to provide the protection of the support material against corrosive reagents which can penetrate through micropores of the coating.

One of the ways of solving the pointed problems is the creation of the composite organo-inorganic layered materials, in particular, based on organic polymers containing additives of inorganic binders, such as polymeric phosphates of aluminium, chromium, zinc, calcium and other metals. The inorganic component provides the high adhesion of the coating to the metal surface as well as anticorrosive protection.

The investigations carried out by us [1, 2] have revealed that incorporation of the metallophosphate binders into the multi-layered composite coatings based on PTFE causes the considerable increasing of their adhesion to steel, aluminium alloys, oxide ceramics. By the way, the high corrosion resistance of coated metallic end-items is achieved.

We have synthesised some new non-toxic binder systems based on aluminium and titanium phosphates, which are compatible with water dispersion of PTFE. It can be supposed that the pointed properties of the phosphate-PTFE coatings are caused with the formation of the microheterogeneous structure of interpenetrating organic and inorganic phases.

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## PROTECTIVE ABILITY and POROSITY of GAS-THERMAL COATINGS

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The outcomes of research of electrochemical and anticorrosive characteristics of gas-thermal coatings of alloys on the iron, nickel, cobalt bases, inclusive an eutectic, composite powders from carbide of a titanium with different bundles, in 15% -s' solution  $H_2SO_4$  are reduced.

It is established that the gas-thermal coatings have identical character of relationship between the velocity of anodic dissolution and the potential. However, the values of critical parameters depending on a porosity and on a composition of coating, describing propensity to passivation, dissolving velocity in a passive condition and potential of transition in area of a repassivation are differed. The period of passivation for coatings occurs faster, than for steel at a minor variation of a potential. The classification of pores on open, open-end and dissipated, which one ambiguously influence on electrochemical characteristics and corrosion resistance of coatings is offered. A distinctive feature of spraying coatings is the weep of corrosion process both on a surface and in a volume of coating, and also on boundary of coating with steel, that promotes intensification of corrosion process resulting in breaking down of a coatings. The value of an open porosity renders dominant influence on protective ability of plasma coatings irrespective of a composition and determines the type of interaction of an electrolyte with coating. The centers of corrosion breaking down are the interparticle and interlayer boundaries, where the main volume of pores is concentrated, and also surface pores, that determines a level of electrochemical characteristics of coating, which one, as a rule, are lower than a level of electrochemical characteristics of compact materials. At value of an open porosity more than 2,5 % the interaction of an electrolyte with a steel undercoat in the basis of pores is dominant and the process flows on boundary with an undercoat, that noticeably reduces protective ability of coating and reduces in its flaking. In this case on potentiostatic curves the stabilization of a current in the field of passivation is not watched. The guard from corrosion breaking down is reached, as a rule at thicknesses of coatings exceeding those for security of an optimal complex of physicomachanical characteristics.

THE INVESTIGATION OF PROPERTIES OF COATING FROM  
FE-NI-B ALLOY OBTAINED BY LASER IRRADIATION.

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The important scientific technological problem is the increase of the lasting and the reliability of the machines and mechanisms details work. Among the perspective directions of the decision of this task by the creation of coating having higher physical-mechanical properties the technology of laser built-up welding have been receipted development.

The purpose of this work is to reveal of conformity of natural laws of influence the technological regimes of Fe-Ni-B alloy facing on physical-mechanical properties of obtained coatings. The processing are made by technological CO<sub>2</sub>-laser with various power density of irradiation and velocity of laser beam moving.

Structural-phase investigations are made by diffractometer DRON-3M. The analysis of the coatings rentgenograms is showed the hard-faced coating structure have been both the amorphous and crystalline structural component. The hard-faced coatings obtained under cooling speed about  $10^4$ - $10^5$  grad/s have on the whole the crystalline structure and it consist from hard solution of iron (Fe,Ni)<sub>3</sub>B on basis tetragonal lattice of nickel boride Ni<sub>3</sub>B ( $a = 0,863$  nm;  $c = 0,437$  nm). There are the microfields of amorphous structure contacted with boride in higher surface layer. Its part is depended on the technological parameters of the treatment.

The corrosion tests of obtained coats are carried out. The anode and cathode curves of each specimens are took off by potentiometer. The corrossions speed for different medium are determinated.

The wear tests of the experimental specimens by the dry friction method are made. It is established the wear value have been decreased under decreasing of the laser beam moving and decreasing of volume powder gave to treatment zone.

The investigation results are showed the laser coatings from Fe-Ni-B alloys were applied worth while for details working in normal and feeble alkali mediums on the abrasive wear conditions.

### THE FORMATION FEATURES OF ELECTRODISCHARGE SILVER COATINGS ON Cu AND ALLOYS ON ITS BASE

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At electrodischarge coating (EDC) erosion fracture of the surface of a workpiece connected as cathode precedes to deposition of coating on that one, then the melt portions transported from the anode consistently interact with the material melt in the cathode voids and at last the top layer composition practically corresponds to the anode composition. However, if on Cu cathode the formation process of silver coating occurs reasonably easily, application of brass or bronze substrates essentially makes the problems more difficult, since in this cases cathode components with high vapour elasticity (for ezample, zink or brass) or stressed state of cathode material (for example, БрБ-2) inhibit to the Ag deposition owing to that significant part of disharge energy is spent for its annealing and this results in decrease of ionized particles density at the cathode.

Quantitative significances of the anode erosion, the cathode weight gain and coefficient of the mass transfer at EDC with casted silver electrodes on the substrates from copper M1, brass Л1-62, bronze БрБ-2 including with previously coated on them electrodischarge Ni interlayer are shown. Availability of the intermediate Ni interlayer is shown to intensifys the mass transfer on the Cu and БрБ-2 substrates. At the same time at electrodischarge Ni interlayer coating on brass the surface is appreciably enreached by Zn that much more deteriorates the formation conditions of the silver coating on it.

Using a scanning electron microscopy a morphology of the electrodischarge Ag coatings on Cu and alloys on Cu basis substrates, the microstructure and the elements distributionon on the cross-section from the cathode basis to the coating surface are investigated.

ELECTRIC - SPARK AND LASER WEAR RESISTANT COATINGS  
BASED ON COMPOSITE CERAMICS OF "TITANIUM REFRACTORY  
COMPOUND - ALUMINIUM NITRIDE" SYSTEMS

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High level of physical - mechanical properties of the titanium refractory compounds in combination with high both heat - conductivity and corrosion resistance of the aluminium nitride allows to consider the "titanium refractory compound - aluminium nitride" system as perspective composite ceramics including the protective coatings deposition.

Formation mechanism, structure and properties of the electric - spark and laser coatings based on TiCN - AlN, TiB<sub>2</sub> - AlN, TiN - AlN on WC - Co, titanium and nickel alloys, carbon and alloyed steels were investigated. The electrode materials for electric - spark alloying (ESA) have been fabricated by powder metallurgy process. Metallographical, XRD and EPMA analyses of the electrode materials and coatings were carried out. Their corrosion and tribological properties were studied. Structure and phase composition of the ESA - coatings considerably differed from those of the electrode materials due to decomposition and oxidation of the electric - erosion products under conditions of spark discharge action. Laser coatings formed as a result of liquid - phase sintering of the powder composite at the treated surface. Their structure and properties were near to those of a solid material manufactured under usual sintering conditions.

The ESA of WC -Co (6%) and titanium VT6 alloys decreases their liner wear by 33% and 60% accordingly, for carbon and alloyed steels - more than by order; simultaneously the friction coefficient decreases, especially for great treatment velocities. Herein the resistance to high - temperature oxidation of coatings increases. In particular the working temperature of coated WC - Co (6%) alloy increases by 160° in compared with the initial surface due to formation of Al<sub>2</sub>TiO<sub>3</sub>, FeAl<sub>2</sub>O<sub>4</sub> high - temperature compounds creating the protective scale film.

Side by side with ESA and laser alloying the materials developed may be recommended for use as the scattering targets in different methods of gas - phase deposition.

**COMPOSITE FIBERS C-BN**

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At present there is a strong interest in development of ceramic fibers with protective coatings. The coating is needed for increasing fiber resistance to oxidation and bonding interaction with ceramic or metal-ceramic matrix. Boron nitride is candidate for coating technology because of its elevated corrosion resistance at high temperatures in different media.

In this work we present the experimental results on production of carbon fibers coated by BN. A procedure includes a nitridation of a cellulose hydrate non-woven material and boron compounds. The material with fibers 30-40  $\mu\text{m}$  in diameter was soaked with ammonium borate or boric acid and then was exposed to previous heat treatment in neutral medium for 1 hour. The reaction was conducted in a nitrogen flow at 1450°C. The products were tested by means of chemical analysis, X-ray diffractometry, scanning and transmission electron microscopy.

The reaction ceased in 2-3 hours at both variants of soaking. Boron oxide in resulting products was not revealed. Within the limits of experimental error, the constant content of boron nitride was achieved for each soaking: 50% mass for ammonium borate and 70% mass for boron acid. The addition of lithium hydroxide to ammonium borate allows an increase in BN yield.

As a result of the nitridation we obtained a material denser than starting one. It consists of fibers 12-15  $\mu\text{m}$  in diameter. Each fiber is a composition of turbostratic carbon and graphite-like boron nitride grains in a core coated by 1.5-2  $\mu\text{m}$  BN layer. The grain size in the core is less than 6 nm. The BN content decreases towards the fiber center.

For testing, the material obtained was oxidized in air at 650°C during 30 min. Destruction of the coating was not observed, but an etching occurs at fiber-ends.



# ADHESION OF CONTINUOUS SiC FIBER AND PHENOL-FORMALDEHYDE RESIN.

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For development of fiber polymeric matrix composites it is necessary to take into consideration the adhesion value of matrix and fiber. Authors investigated adhesion of continuous SiC fiber and phenol-formaldehyde resin.

One of the important characteristic of adhesion is adhesive strength [1]. Quantitative characteristic of adhesive strength was determined by shear strength measurement method. According to this method the SiC fiber sample was placed into cell with phenol-formaldehyde resin and was polymerized. whereupon a sample was investigated with tensile strength machine. Measurements of the pulling strength of SiC fiber from resin let us to determine adhesive strength according to equation:

$$\tau = \frac{F}{S} \quad (1)$$

where F is pulling strength of fiber, Kg

S is surface area of SiC fiber that was placed into phenol-formaldehyde resin, mm<sup>2</sup>

Test results showed that adhesive strength of SiC fiber and phenol-formaldehyde resin is equal to 38-51 MPa (as a function of surface area of SiC fiber that was placed into phenol-formaldehyde resin, Fig.1 )

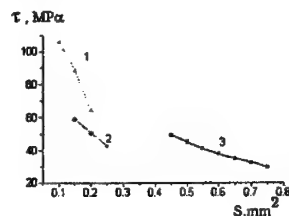


Fig.1 Adhesive strength of SiC fiber and polymer matrices: 1-EDT-20 resin [2], 2-K-21 resin [2], 3- phenol-formaldehyde resin.

Conclusion: Adhesive strength of SiC fiber and phenol-formaldehyde resin is equal to 38-51 Mpa.

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# **THE SHEAR STRENGTH OF THE ZIRCONIA CERAMIC — METAL BRAZED JOINTS**

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The samples of the brazed joints of  $ZrO_2$ -ceramic with metal by the method of capillary impregnation of the CuGa melt through the titanium dust layer and by the method of active brazing using the CuSnPb-Ti alloy as a filler was fabricated. The shear strength of brazes was measured, the Weibull plots were built.

### COMPOSITE MATERIAL FOR FRAMEWORKS OF THE INTEGRATED CIRCUITS.

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The purpose of work is the creation of composite material capable to form at welding by pressure with switching conductors from copper stable, not inclined to brittleness adhesional seams.

The results on development of composite materials intended for use as materials for frameworks of the large integrated circuits are given.

In technology of assembly of the integrated circuits the most responsible and labour-consuming operation is the formation of electrical connections between contact platforms of a microcircuit and taps of the casing, provided, as a rule, welding. The increased demands are made to welded contacts of the integrated circuits.

The physical processes of formation of adhesional seams between a material of a substrate and copper are investigated at welding by pressure.

It is shown, that the introduction in a superficial layer of substrate material of the small additives of chemically active elements can provide reception of stable one-piece electrical connections which are not inclined to brittleness during long operation.

The results of work can be useful by development and improvement of technological formation ways of cohesive and adhesional seams.

## PERFECTION OF MANUFACTURING PROCESS OF TITANIUM-STEEL BIMETAL.

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The results of researches on development of titanium-steel bimetal and layered constructional materials, intended for using them as adapters at welding by a melting of details and units from titanium and steel in units of air-space engineering, are given.

Thermocycle endurance of bimetal in an interval of temperatures 300...850 °C is investigated. It is shown, that for stabilization and increasing of thermocycle endurance of bimetal it is necessary to use a copper with the improved physical-mechanical properties as a layer

Using yttrium doped copper (0,02 %) as a layer provide increasing of thermocycle endurance of a composite more than in 2 times, in comparison with thermocycle endurance of composites, in which the layer is made from copper of the marks M1 or M0b.

Manufacture of titanium-steel bimetal on the vacuum mill DUO-170 is mastered.

The trial-industrial parties of composite material are made that use the microalloyed copper and niobium as damping and barrier layers.

The physical-mechanical properties and serviceability of composites in trial constructions are investigated.

The developed materials are protected by the patents of Ukraine and Russia.

**Influence of scandium on hot-shortness while welding and on  
Mechanical properties of welded joints in alloys of Al-Zn-Mg-Cu  
system**

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Among aluminium alloys the alloys of Al-Zn-Mg-Cu system are the most high-strength which make them a very attractive construction material. But the increased tendency to the formation in welded joints of hot cracks, significant softening of the principal metal in welding process hinder using alloys of this alloying system in welded constructions.

There are produced the experimental alloys of the given system with various level of modification by transition metals, among them by scandium. Sheet semi-products of alloys which don't contain scandium have a partially recrystallized structure. The structure of alloys containing 0.2% of scandium is not recrystallized. The additive materials for their welding are fabricated. The influence of scandium additions to the principal metal as well as to the material of additive wires on the mechanical properties of welded joints as well as on the tendency to the formation of hot cracks is investigated. It is noted a positive influence of scandium on the structure of the ZTHI: refining grains of the principal metal and more uniform distribution of intermetallic inclusions, reducing the recrystallization zone.

The additions of scandium in the amount of 0.2% to the principal metal of an alloy of Al-Zn-Mg-Cu system as well as of 0.5% to the additives from alloys of Al-Mg system are established to allow an increase in the resistance to the formation of hot cracks while welding as well as in the strength of welded joints by 10% in comparison with the variant without scandium.

# CHARACTERIZATION OF THIN FILM COATINGS ON THE SURFACE OF POROUS SILICON

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Complex of Auger electron spectroscopy (AES), thermostimulated exoelectron emission (TSEE), mass-spectrometry (MS), low-frequency dielectric spectroscopy (LFDS) and electron paramagnetic resonance (EPR) methods have been applied to study the chemical composition at the surface that plays a decisive role in light-emitting properties of por-Si. The studies were done on the composition of por-Si real surface, i.e., obtained in the result of electrochemical etching and further contact with gaseous atmosphere. The Auger spectra of por-Si indicate the existence of phases containing silicon or  $\text{SiH}_x$ , oxygen and carbon - amorphous and polycrystalline  $\text{Si}_x\text{O}_y\text{C}_{1-x-y}$  thin film coatings, with effective thickness defined as 1.7-4.1 nm, as well as the background impurities of chlorine, fluorine and nitrogen. Besides, TSEE, MS under electron irradiation and LFDS data give evidence that real surfaces' layer of por-Si reveals the dielectric nature. The intense maximum, the origin of which is the presence of adsorbates on the surface of por-Si is typical for TSEE spectra only at the first heating and is almost absent during the repeated heatings. Further peaks at TSEE spectra appear only after electron beam irradiation of por-Si on contrary to TSEE spectra from clean Si surfaces without oxide coatings [1]. The peculiarities of charge carrier transport and relaxation by localized states were studied by LFDS. The samples of por-Si reveal poor paramagnetic properties. After thermal treatment in vacuum at 670-720 K the complete quenching of luminescence is observed while the EPR signal appears. The EPR spectrum was similar to the spectrum of broken Si bonds in the bulk of amorphous  $\text{SiH}$  or dangling Si bonds at the surface of the crystalline silicon.

- [1] P.V.Galiy, T.M.Nenchuk, and J.M.Stakhira, Thermostimulated Exoelectron Emission Studies of Porous Silicon, *Phys.Stat.Sol. (b)* **212**, R5 (1999)

**MICROSCOPICAL THEORY OF THE BIMETALLIC INTER-  
FACE THERMODYNAMIC PROPERTIES: 3. ADHESION  
ENERGY OF THE SPHERICAL INCLUSION AND MATRIX**

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In framework of the manyparticle self-consistent theory and psedo-potential conception the expression for energy of bimetallic system of the spherical inclusion and matrix for any order of the pseudopotential perturbation theory has been obtained. In second order the adhesion energy of the spherical inclusion and matrix has been calculated. The adhesion energy in terms of the surface energy of spherical metal particle, surface energy of spherical void in metal matrix and "interfacial energy" of the inclusion-matrix system has been expressed. The full self-consistent systems of equations for description of the electronic and ionic structures of the metallic particle, spherical void in metal matrix and for inclusion-matrix system have been obtained. In second order of the pseudopotential perturbation theory the expressions for surface energy of the spherical particle, for surface energy of the spherical void in metal matrix and for "interfacial energy" of the inclusion-matrix system have been obtained. For all enumerated thermodynamic functions the pair interparticle interactions and correlations taken into account. The surface energy of the metal particle, surface energy of the spherical void in metal matrix and "interfacial energy" have size dependence. All results are suitable for bimetallic inclusion-matrix system in arbitrary phase state (solid, liquid, amorphous).

## MICROSCOPICAL THEORY OF THE BIMETALLIC INTERFACE THERMODYNAMIC PROPERTIES: 2. INTERFACIAL TENSION OF TWO LIQUID METALS

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On the basis of the manyparticle self-consistent approach in theory of the inhomogeneous metals and scaling transformation the expression for interfacial tension between two liquid metals in second order of the pseudopotential perturbation theory is obtained. The pair interparticle interactions and correlations in bimetallic system taking into account. The contributions in interfacial tension are expressed in terms of the ion distribution function and potentials of the interparticle interactions which screening effects in inhomogeneous electron gas taken into account. Model calculation with use of the Kirkwood-Buff model of the interfacial structure are made. Numerical calculations for miscible (Na-K) and immiscible (Na-Al, Na-Zn, Cs-Li) liquid metal pairs are executed. Heine-Animalu-Abarenkov and Ashcroft model pseudopotentials are used. For miscible metals (Na-K) the interfacial tension have small positive value for Heine-Animalu-Abarenkov pseudopotential and small negative value for Ashcroft pseudopotential. For pair of immiscible metals (Na-Al, Na-Zn, Cs-Li) the interfacial tension have large positive values. The interfacial tension is very sensitive thermodynamic function to stratification effect.



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**SEMINAR D.**  
**BEHAVIOR AT MECHANICAL LOADING**

**111-124**

## STRUCTURAL SENSITIVITY OF MECHANICAL PROPERTIES OF HIGHPOROUS MATERIALS

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Highporous materials show a number of interesting features due to their porous structure and open a wide range of applications. The following list includes the most interesting properties of highporous materials that are of importance for users in cosmic space, aircraft and transport application. The main of this properties are low specific weight, high specific stiffness, high energy absorption capacity during plastic deformation, reduced thermal and electrical conductivity, good mechanical and acoustic damping and not inflammable.

Design of the materials with high specific strength is one of the most actual problems in material science. In this connection the creation of new composites with low weight and high strength is paid great attention. Usually introduction of light components in a compound permits to diminish weight of the material without diminution (and with increase) of its strength.

To increase reliability of structural elements of materials the special significance has a problem of magnification of rigidity of the elements without magnification of their weight. This problem decides with the help of applications of new perspective materials - porous laminated composites (PLC) with an optimum structure. PLC represents the sandwich structure where high porous layer is surrounded by layers of compact material.

To elaborate optimum structure of porous laminated composites possessing less weight and high resistance to bending load next points should be executed:

1. The optimization of microstructure and properties of compact and porous layers (structural component of laminated composite) as system of grains of different phases.
2. The optimization of structure and properties of porous layer (structural component of laminated composite).
3. The optimization of laminated composite macrostructure as system of compact and high porous layers.

Highporous materials are widely used in energy absorbing structures. The possibility of controlling the behaviour of stress and strain by an appropriate selection of matrix material, porous morphology and relative density makes its as ideal material for such application. Decisive for the quality of impact protection or energy absorber is the feature of being able to absorb energy without the maximum stress or the highest occurring acceleration exceeding the upper limit at which damages or injuries occur. Compared to compact materials, highporous metals are more optimal. In this report structural optimization of highporous foams was elaborated with taking in to account structural theory of work hardening.

**CONCEPTUAL PROBLEMS OF CLASSIFICATION STRUCTURAL -  
PHASE CONDITION OF ALLOYS AT DISSIPATION OF POWER  
INFLUENCE IN ABRASION WEAR.**

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The analysis of a surface friction details of machines subject intensive abrasion wear, accompanying by shock and superficial deformations, mechanical activation and other external power influences has allowed to reveal occurrence special nonequilibrium structural - phase condition of an alloy with significant change physics, mechanical, crystallographic and other properties. In some cases of formation such structural - phase of condition, in opinion of a part of the researchers can not be described within the framework of usual thermodynamic system and causes of attraction of the more general thermodynamic theory of irreversible processes. The speech goes about so-called dissipate structures having temporary or spatial ordering in some interval of external parameters as system self-organizing. In too time, the basic opportunity of occurrence of such structures at study of friction and wear process collides with some conceptual problems not allowing to be entered in the standard understanding sinergetic as scientific direction. It is connected that dissipate the structure, within the framework of nonequilibrium thermodynamics should be spatial, open, stationary, convertible, nonequilibrium, endlessly by thermodynamic system formed in homogeneous environment after transition of some critical point - nonequilibrium kinetic of transition, accompanying by formation new agreement of a condition having coordinated interaction of particles of substance. However study abrasion of destruction of details of machines shows, that the nature of processes occurring in superficial layers of metals at deformation, is connected to usual phase transition proceeding up to a critical point kinetic of transition to agreement to a condition. Besides any microvolume of the deformed metal has non-stationary, not convertible and the more so un-homogeneous structure, dynamics of which wear is connected to increase configuration entropy caused plastic deformation, microcutting and at the end by destruction of metal.

Thus, indication by some researches on an opportunity of formation in alloys subject intensive abrasion wear dissipate of structures requires, on the one hand of deeper and complex proof and with another - decision of conceptual problems at the expense of expansion general classification of the observable phenomena in structure of alloys after strong power influence on principles metastability structural - phase of transitions ensuring dissipation of external energy in frameworks pseudo dissipate systems.

**NEUTRON DIFFRACTION MEASUREMENTS FOR THE  
DETERMINATION OF RESIDUAL STRESSES IN MMC TENSILE  
AND FATIGUE SPECIMENS**

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The experiments here described have been carried out in the framework of a more general research, aiming to develop a set of complementary models to predict the in-service performances of particulate reinforced MMC automotive and aeronautical components. As MMCs are highly heterogeneous materials, residual stresses are present in both the matrix and the particles microstructure, prior to any macroscopic loading. They vary with the temperature and with the type and level of loading imposed to the material, having a strong influence on the mechanical behaviour of MMCs. Neutron diffraction measurements have been performed at the ILL (Grenoble, F), Risø (Roskilde, DK) and HMI-BENSC (Berlin, D), for the determination of residual stress in AA2124+17%SiCp and AA359+20%SiCp specimens, submitted to tensile and fatigue tests. For each of the investigated samples the macrostress has been separated from the elastic and thermal mismatch microstresses [1].

Results show that, in general, the main contribution to the stress state of both matrix and reinforcement is given by the thermal microstresses, already existing due to heat treatments prior to mechanical tests.

[1] M.E.Fitzpatrick, M.T.Hutchings, P.J.Withers, *Acta Mater.* Vol.45, No.12 (1997) 4867.

DISCREET LEVELS OF STRENGTH AND DURABILITY  
OF POLYMER FIBERS AND FILMSE.M.Kartashov, V.V.Shevelev, B.Tsoi

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Supermolecular microheterogeneity of structure of polymer materials is the cause of local over stresses and formation of different types of defects (submicrocracks, microcracks) in their structure, which define their strength. Each type of defects has a corresponding level of breakage stress (or its own durability) on the curve of distribution of strength (durability). The level of strength must be understood as a more or less clearly manifested value of strength near which the samples of material containing defects are grouped. This phenomenon was observed in non organic glasses and glass fibers and later in polymer fibers and films [1]. On the basis of study of statistical distribution of strength and durability of polymer samples several conclusions were made: 1) the existence of corresponding discreet levels is the common property for polymers due to complexity of their structure; 2) the differentiating feature of the function of strength distribution and durability is the poly modality as the outcome of the presence in the samples of materials of defects of different nature. In this case at processing of experimental results on long strength we suggest to go from intermediate values to the more probable, corresponding to the extremum of distribution function; 3) with the change of the applied stress and scale factor there takes place the redistribution of samples according to the levels of strength and durability, characteristic of the given material; 4) the mechanism of failure of massive (low strength) and thin (highly strong) polymer samples (films, fibres) strongly differ.

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**LOADING MECHANICS  
OF ELASTOMERIC COMPOSITE MATERIALS  
OF CONSTRUCTION PURPOSE**

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Improvement of majority of articles created by mankind, including elastic tyres, is marked by the achievements in the field of materials, predetermining new constructive and technological decisions for their realization.

Today the most widely-spread material in tyre industry is rubber which, from the point of view of loading mechanics, is a two-component elastomeric composite material (ECM) of elastic (highly-deformed) matrix and hard (not deformed) particles of the filler, its geometry approaching the sphere. Contribution of rubber is limited, as a rule, by subsidiary function of load redistribution. Special bearing (force) elements are used for load perception.

Creation of three-component elastomeric composite materials of construction purpose results in essential decrease of reasons for majority of technical problems.

They (ECM) contain elastic (highly deformed) matrix and filler particles combination – hard (not-deformed) particles, their geometry approaching the sphere, and pliable (deformed) ones, their length many times exceeding diameter. Ability not only to mechanical load redistribution, but to load perception as well creates prerequisites for possibility to exclude from application of any special bearing construction elements in elastic tyres.

Modifying of loading conditions, modelling stress-strain state of elastic tyres in statics and dynamics, allowed to reveal determining for ECM construction indices, their modifying character in time allowed to reveal the following peculiarities:

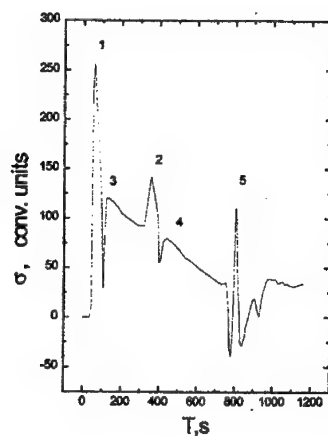
- effect of step formation, which is chiefly the result of presence of pliable (deformed) particles of the filler, their length exceeding many times the diameter;
- effect of structure modifying, which is mainly the result of presence of the filler particles as such.

# SPONTANEOUS RESPONSES OF THE METALLIC GLASS TO IMPULSE MECHANICAL INFLUENCE

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A number of materials (in particular, amorphous metal alloys) react to impulse mechanical influence in a specific way. Such materials are able to memorize, to save and to give back the information about the impulse mechanical influence under definite conditions. The information is represented as characteristic signals of spontaneous response type. These signals contain information about dynamic and energy parameters of active structure complexes determining characteristic features of the investigated materials (electronic, magnetic, mechanical etc. properties).

We have first investigated experimentally spontaneous responses (3,4,5 on the figure) that appear as a result of the influence of two consequent mechanical stress impulses (1,2 on the fig.) in amorphous alloy  $\text{Ni}_{80}\text{P}_{20}$ . The appearance of signals 3 and 4 after the end of impulses 1 and 2 is considered to be connected with the phenomenon of coherent spontaneous creep in an amorphous alloy. The signal 5 arises as a spontaneous response to the result of the consequent influence of impulse 1 and spontaneous signal 4. The observation of these spontaneous responses is a new type of amorphous material spectroscopy.



# INFLUENCE PHASE STRUCTURE OF A MATERIAL TO PROCESSES FATIGUE DESTRUCTION AT A SLIDING FRICTION.

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The understanding and description of the phenomenon of fatigue wear have gained significant progress recently. In process fatigue wear, we have that the kinetics of steady state friction are characterized by regular periodic changes of the friction surface electron work function integral value [1].

The period, amplitude and harmonic contents of such changes are determined by properties of materials and testing conditions.

The experimental researches have shown that a harmonic content of such oscillations essentially depends on phase structure of a material. In case of single-phase (homogeneous) materials the monoharmonic periodic changes of work function rubbing surface are observed, and in case of multiphase materials (heterogeneous) the polyharmonic changes are observed.

The experimental studies have served to construct a physical model of fatigue destruction of a surface layer induced by severe sliding friction.

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### INFLUENCE OF PULSE STRENGTHENING OF PRODUCTS ON THE FORMING OF RESIDUAL STRESSES

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The pulse action of high-concentrated energy flows for coatings which have a high hardness, wear resistance and corrosion resistance.

With the purpose to study the question about possibility to regulate residual stresses in this work the regularities of their formation during pulse strengthening were investigated, the influence of treatment regimes, of the state of product surface and of technological media in their formation was determined.

An pulse strengthening was realized by means of electrosparc alloying (ESA), laser treatment (LT), frictional strengthening treatment (FST) and electroultrasound treatment (EUST). For ESA and LT the prevailing factor, which influence on forming of residual stresses is temperature one. High speeds of heating and cooling of a metal in the elting zone cause the appearance of the thermal stresses which are caused by the difference of values and coefficients of metal linear expansion. In this cases in surface layers residual stresses of tension appear.

It was estimated that the stresses can be regulated by the variation of temperature fields with treatment conditions. For example, in the case of ESA the energy of pulse acts essentially on temperature conditions of coating formation. With the increase of pulse energy from 1 to 6 Joules the thickness of coating increases more than in two times. Residual tensile stresses decrease in two times. The combined treatments ESA+EUST, ESA+LT create in surface layers products more satisfactory structural stressed state than each pulse treatment separately.

## BEHAVIOR OF POWDDER ZIRCONIA MATRIX AT MECHANICAL STRESSES

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The stabilized zirconia in combination with a other oxides has been using wide enough in composites as matrix and as filler as well. Now  $Zr_2O$  has been investigating intensive as inert matrix in composition with armoury plutonium. But zirconia powders behavior at the composite compacting has investigated extremely poorly.

The aim of work is investigation of the high hydrostatic pressure influence at compacting in the 100-1000 MPa interval on structure and phase content of the  $ZrO_2$  - 3 мол. %  $Y_2O_3$  powder system with 12,5 and 18 nm size of the crystalline particles. The coherent dispersion area (CDA) and phase content of the initial powder and compacts has been investigated by X-ray structure analysis method.

It was established that in the powders with tetragonal structure the tetragonal to monoclinic (T→M) phase transformation takes place at hydrostatic pressure. In this case M-phase quantity increase in both powders with pressure growth and increase of particles size. The observing phase transformation is result of the shear stresses and do not connected with influence of the pressure as thermodynamic parameter. It was found that critical pressure of the monoclinic phase appearance depends also on the particles size.

On base of elasticity theory of the anisotropic solid with the non-uniformities it was shown that non-uniformities presence (pores, filler particles) leads to the formation of the local fields of shear stresses proportional to cube of the matrix phase particles. The calculations give quantitative and qualitative agreement with experimental dependence of compacted powder phase contents on powder particles size.

# INFLUENCE OF MECHANICAL AGING TO PROPERTIES OF CERAMICS $ZrO_2 + 3 \text{ MOL. \% } Y_2O_3$ .

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Initial ceramic samples had 3-point bending strength -  $\sigma_f$  and fracture toughness -  $K_{Ic}$  under 3-point bending of a notched sample 720 MPa and  $8,8 \text{ MPa}\cdot\text{m}^{1/2}$ , accordingly.

To find the influence of mechanical aging the following experiments were made. Samples for tests were loaded with speed of 0,005 mm/min up to loading appropriate to stress 450 MPa and were maintained under this loading within 15 hours. Then samples unloaded and at speed of 0,5 mm / min was measured  $\sigma_f$ . Notched samples on the same technique were loaded up to  $K_I$  (see table) and were maintained at given  $K_I$  within 6 hours. After its unloading the  $K_{Ic}$  at speed of 0,5 mm/min was measured. In all experience values of  $\sigma_f$  and  $K_{Ic}$  averaged on five measurements.

It is revealed, that the mechanical aging results to increase of mean value  $\sigma_f$  up to 830 MPa. The dependence  $K_{Ic}$  from  $K_I$  is shown in the table.

$K_I, \text{MPa}\cdot\text{m}^{1/2}$	2,51	4,7	5,84	6,18	6,33	7,13	8,31
$K_{Ic}, \text{MPa}\cdot\text{m}^{1/2}$	8,91	9,79	11,26	9,83	11,07	12,13	12,5

It is known [1], that  $\sigma_f$  and  $K_{Ic}$  are more than more size of transformation zone (zone, where under an operation of affixed stress the transition of a tetragonal phase in monoclinic happens, i.e. happens the transformation toughening). This means, that the endurance under loading promotes to increase of transformation zone, and, hence, its formation and growth have a kinetic nature. On the basis of representation that to implementation of martensitic transformation of a tetragonal phase in monoclinic is necessary create nucleus of a new phase of the critical or supercritical size the discussion of observed effects are carried out.

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### INFLUENCE OF PLASTIC DEFORMATION AT HIGH HYDROSTATIC PRESSURE ON PROPERTIES OF METAL- MATRIX COMPOSITES

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The using perspectives of composite materials from non-ferrous metals and alloys on their basis allow to increase of heating-resistance, corrosion-resistance, vibro-resistance and other properties, that gives one possibility to increase the reliability level and longevity of details and constructions at lowering of their specific gravity. However, the low plasticity and the use of deficiency of raw material for producing of metal-matrix composites in traditional technologies decreases essentially the field of their application.

One of the prospective method of obtaining of such materials is application of casting technologies, allowing to vary the form and size of articles into the wide range.

In this work the influence of plastic deformation at high hydrostatic pressure conditions on structure and properties, plasticity and porosity of aluminium alloys A97 and Al2, saturated by dispersible strengthening particles of  $Al_2O_3$ ,  $TiO_2$ , SiC with the total volume ratio up to 0.2% obtained by special casting, allowing to regulate of initial porosity ( $\Theta=40-10\%$ ) has been studied. The settling under pressure, hydroextrusion and hydrostatic dynamic extrusion with the deformation rate  $\dot{\Psi}=40\ldots90\%$  into the temperature range  $20\ldots600^\circ C$  were used as deformation methods.

The strengthening curves have been obtained and their quantitative measurement according to Hollomon's equation allowed to reveal the deformation strengthening stages have been realized.

The experiments have been carried out and influence of distribution and porous sizes on deformation and viscous failure of aluminium alloys have been determined.

# INFLUENCE OF SILOCON CARBIDE SPECIMENS DIMENTIONS UNDER ONE AXIS PRESSING STRENGTH ESTIMATION

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Experimental estimation of dependence press strength boundary  $\sigma_c$  from specimen dimentions is need for scientific prognostication silicon carbide goods quality under press strain. Such research were made for silicon carbide by Brovary powder metalurgy plant, according method, described [1]. Manufactured by diamond tools spacimen dimentious and investigations results you can see in table, wich are presented in grap coordinate  $\ln \sigma_c - \ln V$ . The fact of correlation experimental results and

Dimension specimen, mm	Volume V, cm <sup>3</sup>	$\sigma_c$ , MPa
4,5x6,0x18	0,49	1984 (1756)
10x10x30	3,00	1810 (1795)
9x15x36	4,86	2164 (1805,2085)
15x24x72	25,92	1382 (1527)
15x48x80	57,60	1416 (1318)

properties of porcelain ceramic [2] established, and they are approximated by the use linear - broken functions  $\ln \sigma_c \sim k \ln V + b$ , where  $k$  and  $b$  - accordingly, the proportionaliti

coefficient and a line the cut on ordinate axis.  $k$  and  $b$  parameters were calculated by the least square methode. After mathematical transformation the equation dates are:

$$\sigma_c \sim e^{7,48} \cdot V^{0,012}; \text{ by } 0 < V \leq 4,86 \text{ cm}^3; \quad (1)$$

$$\sigma_c \sim e^{7,96} \cdot V^{-0,185}; \text{ by } V \geq 4,86 \text{ cm}^3, \quad (2)$$

where  $e = 2,71828$  - the base of logarithms.

In table, the round brackets means of  $\sigma_c$  calculated according formulas (1) and (2). The point of cross pependences (1) and (2) is meaning  $\sigma_c$  for  $V = 4,86 \text{ cm}^3$ , and both dependences (1) and (2) are correct simultaneously.

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# THE PRESSING AND BENDING STRENGTH AND INTENSITY OF STRAIN COEFFICIENT FOR BORON CARBIDE ESTIMATION

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The module elasticity  $E$ , one axis pressing strength boundary  $\sigma_c$ ,  
bending strength  $\sigma_{3r}$ , and intensivity strain coefficient  $K_{1c}$ , as the cracking  
resistance quality, were definite for 5 experimental types boron carbide in  
according to methodes [1, 2]. The data of table were presented in graph  
coordinate  $\ln K_{1c} - \ln \sigma_c$  and  $\ln K_{1c} - \ln \sigma_{3r}$ . As it appears, these  
dependences approximate with straight lines equations:

$$\ln K_{1c} \sim k \ln(\sigma_c, \sigma_{3r}) + b,$$

where  $k$  and  $b$  - accordingly, the proportionality coefficient and a line of  
the cut on ordinate axis.  $k$  and  $b$  parameters were calculated by the least  
square method. After mathematical transformation the equation dates are:

$$K_{1c} \sim (\sigma_c, \sigma_{3r})^k \cdot e^{-b},$$

where  $e = 2,71828$  - the base of logarithms.

Material	$E \cdot 10^5$ , MPa	$\sigma_c$ , MPa	$\sigma_{3r}$ , MPa	$K_{1c}$ , MPa·m <sup>0,5</sup>
Boron carbide 1M	3,40	1730 (2,28)	142 (2,52)	2,53
Boron carbide 2M	3,89	4880 (4,71)	343 (4,52)	4,27
Boron carbide 3M	3,36	4290 (4,29)	325 (4,36)	4,53
Altynete	2,83	3950 (4,05)	247 (3,64)	3,40
Carboride	4,27	5410 (5,05)	257 (3,74)	4,56

To definite  $K_{1c}$  by way of  $\sigma_c$ , the parameters of the last equation are:

$k \approx 0,70$ ;  $b \approx 4,41$ . In case, when  $K_{1c}$  is found by way  $\sigma_{3r}$ , then  $k \approx$   
 $0,66$ ;  $b \approx 2,34$ . In table in round bracket means  $\sigma_c$  and  $\sigma_{3r}$  are presented  
 $K_{1c}$  during the last equation.

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### MICROHARDNESS AND CRACKING RESISTANCE OF LaB<sub>3</sub>O<sub>6</sub> SINGLE CRYSTALS.

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Lantan metaborate LaB<sub>3</sub>O<sub>6</sub> - is relatively new, efficient material for detection of thermal neutrons [1]. Mechanical properties of this material have not been investigated.

In present work we asses fracture behaviour LaB<sub>3</sub>O<sub>6</sub> single crystals that occurs during deformation by indentation method.

LaB<sub>3</sub>O<sub>6</sub> single crystals longer than 15 mm and up to 8 mm in the diameter were grown by Czochralski method. Main crystallographic date:  $a=9,946$ ,  $b=8,163$ ,  $c=6,496$  Å,  $\beta=127,06^\circ$ .

Our crystals were cleavage along  $(10\bar{1})$  plane under mechanical deformation. Investigation by optical microscope reveals surfaces of nearly absolute cleavage.

Freshly cleaved  $(10\bar{1})$  surfaces were tested by indentation method (1N load). Microhardnes of 6200 MPa was measured. Strong splitting appears around the impression. Radial crack traces follow to  $[111]$  and  $[11\bar{1}]$  directions. This observation suggests that the  $\{111\}$  planes are also an easy fracture planes in this material.

Coefficient of stress intencity was determined [2] to quantitatively estimate the cracking resistance of lantan metaborate. For LaB<sub>3</sub>O<sub>6</sub>  $K_{Ic}=0,53$  MPa·m<sup>-1/2</sup>. This result indicates that lantan metaborate single crystals is decidedly brittle material.

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**SEMINAR E.**  
**COMPOSITES WITH THE CERAMIC MATRIX**

**126-176**



**PRODUCTION AND PROPERTIES OF CERAMIC MATRIX  
COMPOSITES OF Si-Ti-B-C AND W-Ti-B-C SYSTEMS**

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Regularities of sintering under pressure (HP), structure and mechanical properties of composites of B<sub>4</sub>C- MeB<sub>2</sub>, SiC-B<sub>4</sub>C-MeB<sub>2</sub> (Me - Ti, Zr), W<sub>2</sub>B<sub>5</sub>-TiB<sub>2</sub> and W<sub>2</sub>B<sub>5</sub>-TiB<sub>2</sub>- B<sub>4</sub>C eutectic systems are explored. Composites were received using a sintering of previously synthesized components as well as a regime of reactionary sintering.

It was found that the transition from single-phase to heterogeneous state is accompanied by activation of sintering process, diminution of a grain size and a sharp improvement of mechanical properties (fracture toughness, strength, hardness and wear resistance). A possibility of production of high-strength states (at bending strength up to 800-1000 MPa) in a wide temperature range with the hardness level that characterizes the superhard materials has been shown.

The increase of strength and other mechanical properties of ceramic materials is explained with the aid of thermomechanical model of composites taking into account effect of non-uniform internal stresses fields.

**BIOCOMPATIBLE CERAMIC MATERIAL**

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There are the strong requirements for the medical implant materials. It must be durable, biocompatible, chemically inert with respect to physiological human medium. At present various firms are manufacturing metal, plastic, porcelain, and ceramic implants for stomatologic purposes. However, these substitutes not fully meet the requirements of the World Public Health Organization as some of them are too heavy and the others are insufficiently durable, and are not always functional in relation to the man's organism.

The present work is devoted to developing and studying the properties of biocompatible fibrous aluminium oxide-based ceramics and to possible using in the maxillofacial surgery.  $\text{Al}_2\text{O}_3$  fibres with an addition MgO were employed as starting material to prepare the corundum ceramics.

Aluminium oxide-based fibres were chosen for medical-biological investigations because of their high chemical stability, inertia to biological tissues as well as because of their porosity and capillary permeability. The prepared fibres were crushed, the disk and beam ingots were moulded and sintered at 1500-1600°C. The performed investigations of material structure promoted to developing of the optimal technology.

Alumina ceramics is strong and inert with respect to neutral, alkaline and acidic media. It was ranked among low-toxic and low-hazard substances (IV hazard class according to GOST 12.1.007-76) and did not cause any irritating or allergic effects. Biomedical tests were performed on different animals. An aluminium oxide ceramic implant was inserted in the artificial defect of the mandible. After the definite periods the animals were taken out of experiment and the mandible bone sections were examined by morphological method. The experiment confirmed the regeneration of a bone tissue and after 1 year the formation of the mature bone at the defect place. Results of clinical trials conducted in the Belorussian hospitals testified the perspective of prepared material using for maxillofacial surgery.

## NONTRADITIONAL METHODS OF THE OBTAINING OF REFRACTORY NONOXYGENOUS COMPOUNDS

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The development modern science-capacious of technologies indissolubly is connected to creation of a new class high-temperature materials by produced powder metallurgy methods from nonoxygenous refractory compounds (NRC). However the application similar materials at present is limited, despite of a complex of the important physical-chemical properties inherent in given substances. It is stipulated first of all by lowest degree of reproducibility of their operating performances, that certainly, is connected to a high dishomogeneousness of initial powders. Therefore one from central problems in the field of creation of materials from refractory compounds is the development principally new modes to synthesis of their initial powders, homogeneous not only on chemical and phase composition, but also that most importantly on texture and microstructure of separate particles. For a successful solution of the given problem it is necessary in the beginning to make clear the basic reasons of so high dishomogeneousness of NRC powders, which, doubtlessly, are stipulated both chemical nature of given compounds, and existent methods of their obtaining. The majority of carbides, nitrides, borides and silicides is represented itself phases of a variable composition with a broad variation of Me/X ratio, which properties enough noticeably are altered in the dependence from a phase composition. The variety of structural phases and phases with broad areas homogeneousness, inherent NRC, stipulates inevitability of forming at synthesis of a product unhomogeneous on chemical and phase composition. However basic reason of a dishomogeneousness of obtained in the present time powders NRC is stipulated not by specificity of their chemical nature, and singularities of a passing heterophase of processes of their synthesis. The traditional methods of obtaining NRC in an aspect multistaging heterophase processes of their synthesis in the principal can not supply the forming homogeneous on a composition and microstructure of powders particles.

In the present report are considered on principle new methods of synthesis NRC, in which nucleation and the forming of a product is realized always in a surplus of metal, and the rate-limiting stage is properly the reaction of the compound formation.

### Zirconia Ceramics and their Prospects in Ukraine

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The Ukrainian technologies of zirconia powders and ceramics with high performances are developed. Powders for coatings are also available.

Using

- Zirconium Hydroxide of Vilnohirska Mining & Metallurgical Plant,
- Cold Isostatic Pressing and
- Special Course of Milling, Heat Treatment and Sintering

authors produce ceramics with the World level of properties.

Please find

Properties	Cold Isostatic Pressing	Hot Isostatic Pressing
density, $g/cm^3$	5.77	6.08
Strength, $MPa$	940-1100	1200-1400
Fracture toughness $K_{Ic}$ , $MPa \cdot m^{1/2}$	11-14	16-19
Hardness	11	13
HV, $GPa$		
Color	white	black

Zirconia Ceramics are ceramic steels and may be used in many cases as effective substitutes for metals. Their unsurpassed

- *surgical scalpels, industrial blades, knives,*
- *bearings,*
- *valves, seals and other parts of pumps,*
- *tools to process metals by pressure,*
- *gems*

are demonstrated. They have high market potentials and may be manufactured in Ukraine in industrial scale being based on zircon-sand of the Ukrainian deposit that is the richest in Europe.

***Investors are welcome!***

## SYNTHESIS OF SIALON FROM CAOLINE AND STUDY OF ITS STRUCTURE FORMATION

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The  $\text{Si}_3\text{N}_4$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{AlN}$ ,  $\text{SiO}_2$  and other components (at their different ratio) are traditionally used for sialon manufacturing. However, it is possible to synthesize sialons using the cheap natural materials of caolinite-type as well. Earlier this process was not studied enough. The goal of our research is to manufacture the  $\beta'$ -sialon from caoline, study its structure formation and phase composition under change of synthesis conditions and raw material composition. The Prosyansky caoline, both enriched (KR-2 19608-84) and non-enriched, was used as raw material. The sialon was fabricated from a mixture of caoline and technical carbon in a Tamman furnace in the nitrogen medium. The study of structure formation and phase composition was carried out for different stages of synthesis using the XRD and chemical analysis methods in the temperature range of 1200...1700°C. The one-phase and multi-phase  $\beta'$ -sialons in the wide region of their existence ( $z = 0...4$ ) were obtained by a variation of initial raw material composition and synthesis temperature.

The main regularities of a sialon synthesis mechanism were established. It was shown that the intermediate product of sialon synthesis from caoline was silicon nitride with a further substitution of silicon and nitrogen atoms in its tetrahedra for AlO groups. The concentration of these groups in the  $\text{Si}_3\text{N}_4$  elementary cells that defines a Z number depends on the synthesis temperature and Si/Al ratio in the initial raw material. The intermediate  $\text{Si}_2\text{ON}_2$ ,  $\text{Si}_6\text{Al}_6\text{O}_9\text{N}_8$ ,  $\text{Si}_{12}\text{Al}_{18}\text{O}_{39}\text{N}_8$  and 15R-AlN polytype phases formed under some conditions. The regions of their existence as well as conditions of their conversion into a sialon were established. The SiC forms at the temperatures above 1500°C. It is then reduced by thermodynamically stable intermediate phase, viz.,  $\text{Si}_{12}\text{Al}_{18}\text{O}_{39}\text{N}_8$ , and entirely disappears before a completing of a synthesis process. It was established that the Si losses were determined by SiO evaporation at the initial stage,  $\text{Si}_3\text{N}_4$  dissociation as well as a partial sialon destruction resulting in its conversion into a 15R-AlN polytype. For a certification of sialon powder the procedure of express-analysis (XRD method) was proposed. The results of research carried out can be used as a basis for the industrial manufacture of sialons using caoline.

# THE INFLUENCE SIALON'S PHASE CONSTITUTION AND SINTERING ADDITIVES ON THEIR DENSITY, HARDNESS, AND FRACTURE TOUGHNESS COEFFICIENT

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Phase composition ( $\beta$  and  $\alpha + \beta$ ) of sialons,  $Y_2O_3$  and  $Nd_2O_3$  as sintering additives and their proportions on the density, HV and factor of fracture toughness of sialons have been examined. For the carrying out of the experiment the design  $2 \times 2 \times 3$  has been used. Where 2 - two levels of phase composition ( $\beta$  and  $\alpha + \beta$ ) and two levels of  $Y_2O_3$  (4 and 6%) and 3 - three proportion levels of  $Y_2O_3/Nd_2O_3$  (75/25; 50/50; 25/75).

After working of the experimental results and equation of coefficient valve check the following adequate equations have been obtained:

$$y_1 = 3.25 + 0.04x_2 \quad y_2 = 15.7 - 2.12x_3 - 0.29x_1x_3 - 0.92x_3^2 \quad y_3 = 4.63 + 0.47x_3 + 0.47x_3^2$$

From the equation (1) one can see that in the given case the phase constitution and proportion  $Y_2O_3/Nd_2O_3$  ( $x_3$ ) does not exercise influence on SiALON density ( $y_1$ ) besides  $Y_2O_3$  influence ( $x_2$ ) in the interval 4-6% is not extremely great too.

Analysing the equation (2) one can come to the following conclusion:

1. The greatest influence on HV exercises  $Y_2O_3/N_2O_3$  ( $x_3$ ) proportion. The composition influence is less and tells on  $x_1x_2$  interaction. The influence of  $Y_2O_3$  ( $x_2$ ) content is essential in these intervals (4-6%).

2. To increase the hardness it is necessary to fix the first factor ( $x_1$ ) on the top level ( $\alpha + \beta$ ) and  $Y_2O_3/Nd_2O_3$  ( $x_3$ ) proportion to fix on the lower level, that is 75/25. In this case the rated value is  $y_2 = 17.2 \text{ GPa}$ . It should be pointed out from the equation (3) that the first two factors ( $x_1$  and  $x_2$ ) have not effect on  $K_{Ic}$  and furthermore  $K_{Ic}$  value and its dependence from this relation is expressed by parabola. Maximal value  $K_{Ic}$  ( $y_3$ ) at  $x_3 = +1$  will be ( $Y_2O_3/Nd_2O_3 = 25/75$ ). It is equal to  $5.57 \text{ MPa m}^{0.5}$  (experimental value  $K_{Ic} = 5.75 \text{ MPa m}^{0.5}$ ). Hence the governing factor is the relation  $Y_2O_3/Nd_2O_3$  ( $x_3$ ).

Correlative linkage between all the parameters have been revealed in this work. That provides a way to calculate correlative equations establishing a link between these parameters. On this evidence one can determine the other one every parameters for one  $Hv_{10}$ . Density increase was demonstrated to bring to hardness growth but the first one reduces failure toughness. Aside from  $Y_2O_3/Nd_2O_3$  relation the impact of yttrium oxide to other RE oxides on  $Hv_{10}$  and toughness of failure  $K_{Ic}$  has been studied.  $Sm_2O_3$  additive was demonstrated to make possible higher value  $K_{Ic}$  ( $> 5 \text{ MPa m}^{0.5}$ ) than Dy and Yb oxide additives.

# X-RAY RESEARCH of SYNTHESIZING SIALON FROM KAOLIN by CARBOTHERMAL REDUCTION and SIMULTANEOUS NITRIDING

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Sialons are perspective ceramic materials. For obtaining of sialon' powders take use method of carbothermal reduction and simultaneous nitriding of kaolin or close to it in chemical composition ash from combustion of coal.

Were investigated influence of carbonitriding' conditions of kaolin on phase structure and specific surface of final powders of sialon. Kaolin was preliminarily annealed at temperature 800°C. As the reducing agent was used colloid graphite C-I. The mixture of kaolin and graphite was blended dry in an epicyclic grinding mill "Sand".

Nitriding of mixture was in not flowing atmosphere in chamber volume of 100 litres with the graphitic heater in freely filled or in pressings, obtained at pressure 25-100 MPa.

The base mixtures of kaolin with graphite have high specific surface  $S_{sp} = 24-26 \text{ m}^2/\text{g}$ , the increase of milling' time in "Sand"  $t$  up to 90 minutes has called minor growth of  $S_{sp}$  up to  $28 \text{ m}^2/\text{g}$ , and at increase of  $t$  up to 120 minutes the shock of  $S_{sp}$  till  $70,9 \text{ m}^2/\text{g}$  is observed. The synthesised powders of sialon have considerably smaller  $S_{sp} = 3-5 \text{ m}^2/\text{g}$  and their specific surface is increased at growth of milling' time of base mixture in grinding mill "Sand".

In all modes of synthesising the obtained powders are non-single-phase. Closely to an optimum regime for obtaining mostly phases of  $\beta'$ -sialon are following condition: content of carbon - 18-20%; temperature of synthesising - 1400-1420°C; time of synthesising - 3 h; single portion - 1 g. At more heats there is disintegrating of sialon on phases of silicon carbide and nitride.

At nitriding (1420°C-3h) large single portion (26 g) mixture from kaolin - 24 % of graphite was received J-sialon phase with composition  $\text{Si}_6\text{Al}_{10}\text{O}_{21}\text{N}_4$  with impurity of O'-sialon, that the phase with the low contents of azote is obtained. 15R sialon is obtained on most porous pressings. As a rule, in pressings, the quantity of impurity of  $\alpha\text{-Al}_2\text{O}_3$  is more, than in free filling powder, sometimes the additive of X-phase is watched. The significant quantity of X-phase was obtained at nitriding powder mixture from kaolin - 20 % graphite in environment of dissociated ammonia.

## ABRASIVE COMPOSITE MATERIALS AT CERAMIC BOND

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New instrumental composites for the machining of non-metal materials were developed at the basis of the data, obtained by the study of physico - chemical interaction in contact zone.

Composites are based at  $\text{Na}_2\text{O} - \text{SiO}_2 - \text{B}_2\text{O}_3$  low temperature glass (temperature of transformation lower than  $600^\circ\text{C}$ ), modified with clay mineral - montmorillonite. Formation of new crystalline phases in this compositions is connected with dissolution of hard phase in the melt of glass. Products of dissociation of the montmorillonite layer structure at  $700 - 900^\circ\text{C}$  dissolve partly in the melt, forming strong volume structures, increasing the strength of composite.

Study of processes at glass - montmorillonite contact border at  $700 - 900^\circ\text{C}$  demonstrate the formation of the new phase ( $\text{CaTiSiO}_5$ ), caused by mutual diffusion of components. Taking this into account, there were established optimum correlations between glass and clay mineral. Study of mutual depends between structure of composites and their mechanical strength made it possible to develop new effective diamond tools for grinding of natural stone and synthetic construction materials.



**Structural features of AlN-TiN and AlN-ZrN composites  
obtained by nitriding of intermetallics.**

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The structure of composed materials, particularly the degree of nitriding and distribution homogeneity of phases, determine to a large extent their features. To obtain materials with fine-dispersed homogeneous structure "chemical mixing" is widely used in oxide systems, while in Nitride systems the similar techniques are not developed.

The author of the present paper advanced method of "chemical mixing" of nitride components for obtaining AlN-TiN and AlN-ZrN composites consisting in joint nitriding of elements mixed at atomic level in a form of a regular structure of intermetallics. The nitriding process of compact and powdery intermetallics TiAl, TiAl<sub>3</sub> and ZrAl<sub>3</sub> at 600 - 1300°C in nitrogen and ammonia media was studied.

It was shown that nitriding of ZrAl<sub>3</sub> is followed by aggregation of the forming nitride phases. It inhibits fine and uniform distribution of these phases while for TiAl and TiAl<sub>3</sub> this process is not practically observed at optimum nitriding regime. Study of the TiAl and TiAl<sub>3</sub> nitriding products by electronic microscopy (magnification up to 20000) disclosed that the material is composed of isometric polyhedral crystals of TiN uniformly distributed in the mass of fine needle-shaped crystals of AlN. X-ray analysis also testifies that the reaction products are nitrides, with lattice periods practically not differing from those presented in literature. IR-spectrum of the Ti-Al nitriding product is in fact the super-position of spectra of AlN and TiN which points to absence of interaction between phases.

High dispersity and homogeneity of heterogeneous powder mixtures of nitrides of Al and Ti obtained by nitriding of intermetallics TiAl and TiAl<sub>3</sub> allow to prepare samples from them by sintering in nitrogen medium without imposing pressure. These samples offer high density ( $\gamma > 95\%$ ) and exhibit high strength properties: bending strength 440 and 530 MPa, Rockwell hardness 80 and 83, fracture toughness 5,0 and 6,2 MPa·m<sup>1/2</sup> correspondingly.

## OBTAINING AND PROPERTIES OF A NEW CERAMIC MATERIAL ON THE BASIS OF CHROME CARBONITRIDE

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The basis of solid compounds and ceramic materials applied in industry is known to be the highest high-melting compounds. At the same time, the lowest carbide and nitride phases can be the promising object of an investigation under creation of new materials. We have chosen chrome carbonitrides as a basis of such alloys because they take an intermediate position between chrome carbides and nitrides. In this connection the original new technology (know-how) was developed. It deals with the obtaining of one-phase chrome carbonitrides as hard solutions of carbon in a lattice of the lowest nitride  $\text{Cr}_2\text{N}$ . The investigation of these compounds showed that carbonitrides arrange nearer to the highest chrome carbide than to the lowest chrome nitride, this latter is their basic compounds.

It is found that the most advisable way of obtaining products from the new ceramic material is a new kiln technology. It became possible on the basis of porosity and shrinkage variation in dependence upon temperature and time of baking. The mixture of initial compounds charge applied here consists of the lowest chrome nitride  $\text{Cr}_2\text{N}$ , soot and nickel. Content of the latter corresponds to 10, 15, 20 and 25 mass %.

Mechanical, chemical and tribotechnical characteristics of the new ceramic materials were investigated. It is shown that their maximum hardness reaches 91-92 HRA. Their corrosion resistance is stated to have the first or highest place according to the ten-point scale in sulphuric acid solutions. Besides this, the new ceramic material has high wear resistance, when workload is above 150 H and friction speed is 10 metres/sec. in terms of dry friction in couple with boronated steel 45. These products developed from the new ceramic material were tested and introduced as wear resistant at "Artempolysvarka" enterprise and they were introduced as corrosion resistant at the Institute of problems of Mathematical machines and systems NAS Ukraine experimental plant.

# STRUCTURE AND SOME PROPERTIES OF ZIRCONIUM DIBORIDE FILMS, OBTAINED BY MAGNETRON SPUTTERING

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The  $ZrB_2$  thin films are investigated very small. This can explain a narrow field of their application, in main, as decorative and corrosion stable coatings [1, 2].

In the present work the structure and the electrical properties of the zirconium diboride films are investigated. They were obtained by the magnetron sputtering of hot pressing  $ZrB_2$  targets. The  $ZrB_2$  films were produced in the Ar environment at pressure  $(1-3) \cdot 10^{-1}$  Pa. The current of target was changed in a range 0.6 - 3 A, the voltage - 600 - 800 V.

$ZrB_2$  films with 0.03 - 0.1  $\mu m$  thickness were quasiamorphous. If the film thickness was increased up to 0.2  $\mu m$  the weak maximas were observed on the diffractograms in accordance with the orientation of the coherent scattering blocks by planes (101), (001) and (102) is parallel for the plane of the growth.

Under increase of films thickness up to 0.35  $\mu m$  some change of the blocks primary orientation in films was observed. The growth of the blocks to a direction  $\langle 001 \rangle$  was appreciably increased and decreased to a direction  $\langle 100 \rangle$ .

Under increase of the films thickness up to 0.5  $\mu m$  there was an even more noticeable reorientation of blocks of coherent scattering. On a background of texture growth increase to a direction  $\langle 001 \rangle$  there was the weak texture orientation of a blocks part to a direction  $\langle 002 \rangle$ .

The temperature resistance coefficient (TRC) of the amorphous films was negative. With increase of films thickness TRC was changed the sign. The absolute value of TRC of  $ZrB_2$  films is equal  $10^{-5} - 10^{-6} \text{ grad}^{-1}$ .  $ZrB_2$  films are stable at heating on air. Their noticeable oxidation was begun at to durablis endurance at  $T > 500 \text{ K}$ .

Taking into account high chemical stability, thermal and corrosion stability and also small specific resistance [3] and TRC of films, it is possible to consider their application as perspective as low resistance and contact layers in electronic engineering.

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# KINETICS OF ELECTROCHEMICAL PROCESSES ON SURFACE OF TiB<sub>2</sub>-AlN, TiB<sub>2</sub>-TiN AND TiC<sub>0.5</sub>N<sub>0.5</sub> CERAMICS IN 3% NaCl SOLUTION

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The ceramics of TiB<sub>2</sub>-AlN, TiB<sub>2</sub>-TiN, TiC<sub>0.5</sub>N<sub>0.5</sub> as well as monolithic TiB<sub>2</sub> were fabricated using a HIP method (without additives). In particular, for the TiB<sub>2</sub>-AlN system an average size of initial powders was 5.8 and 2.6  $\mu\text{m}$ , the specific surface value being 0.6 and 2.5  $\text{m}^2/\text{g}$ , respectively. The cycle of isostatic pressing was carried out at 1900°C and 195 MPa during 90 min in argon medium. The samples density was >99%. The microstructure and phase composition of samples was studied by XRD and SEM methods. Anode and cathode behaviour of ceramics samples were studied by potential-dynamic method of polarization curves using a P 5848 potentiostat device under rate of potential change 0.5 mV/s.

It was established that on the surface of all the studied samples, including after their preliminary treatment by grinding, a priori there is a thin oxide film (maybe, an oxygen adsorption layer) that slows down the samples corrosion in 3% NaCl. The film pointed out is reduced by hydrogen atoms (in situ) under their cathode evolution in the same electrolyte at the potentials up to -1.6V (in relation to the chlorine-silver comparison electrode). Practically in all the cases one can observe the hysteresis of straight and reciprocal run of cathode polarization curves. It was established that the corrosion process is multi-stage one. After anode dissolution - with transition of Ti<sup>3+</sup> -ions into solution - the partial formation of TiO<sub>2</sub> (rutile) protective layer takes place, the latter slowing down the dissolution of composite material components. In the case of TiB<sub>2</sub> - AlN, in the final stage the formation of thin AlO(OH) film takes place as well.

It was shown that the corrosion resistance of prepared ceramics samples in 3% NaCl solution is exceptionally high. It only slightly decreases in the row: (TiB<sub>2</sub>-AlN) - (TiB<sub>2</sub>-TiN) - TiC<sub>0.5</sub>N<sub>0.5</sub>. However, in all the cases the corrosion rate of samples of such binary systems proved to be approximately by three orders less than that of pure titanium boride. Therefore we can recommend the ceramics developed for their use as high-performance materials for the exploitation in sea water.

# SELF-REINFORCED COMPOSITES IN THE SYSTEM ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>- CeO<sub>2</sub>- Al<sub>2</sub>O<sub>3</sub>

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The composites in the system ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>- CeO<sub>2</sub>- Al<sub>2</sub>O<sub>3</sub> concern to the new class of materials, which physical and mechanical properties are resulted from joint effect of the matrix from ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>,CeO<sub>2</sub>) and strengthening phase - plates of  $\alpha$ - Al<sub>2</sub>O<sub>3</sub>.

The main objective is to investigate the opportunity of the self-reinforced composite materials producing in the system ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> from the nanocrystalline starting powders.

Nanocrystalline powders are obtained with a combined method of hydrothermal synthesis and sol-gel technology. A size of the powder primary particles was 5 - 10 nm. The powders are assembled in spherical soft agglomerates by a size up to 5 microns. A specific area of powders after heat treatment was 10 - 47 m<sup>2</sup>/g. The phase composition was : T- ZrO<sub>2</sub>,  $\alpha$ - Al<sub>2</sub>O<sub>3</sub>.

Two methods of the starting powders forming are used: cold uni-axial pressing in a metal mould and slip casting of the aqueous slips. Slips characterised by the good foundry properties. The slip liquid phase contents was 30 %. Relative density of green bodies is varied from 0,30 up to 0,45 depending on the forming method.

Green bodies are sintered up to relative density 0,98 - 0,99 at temperature 1300 - 1450 °C under air and vacuum as well. Depending on the green bodies forming method, their linear shrinkage under sintering makes up 24 - 29 %. The material microstructure is: the  $\alpha$  - Al<sub>2</sub>O<sub>3</sub> plates locate in the ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>,CeO<sub>2</sub>) fine-grains matrix. The variation of the obtaining conditions allows to change a size of the  $\alpha$  - Al<sub>2</sub>O<sub>3</sub> plates from proportional to the ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>,CeO<sub>2</sub>) matrix grains (0,3-0,5 microns) up to 12 - 15 microns.

The materials strength behaviors are : bending strength 900 - 1100 MPa, K<sub>1c</sub>=12- 18 MPa.m<sup>0,5</sup>.

These materials are perspective for manufacturing of the cutting tools (scalpels, knives, scissors); abrasive resistant details for textile fibres production; dies for sputtering of abrasive materials.

### Synthesis of Nanosize Zirconia (3Y-TZ) Powder with Narrow Particle Size Distribution by Oxalate Processing.\*

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Zirconia is one of the most promising material for structural and functional application. Particle size, shape, distribution, and morphology are important factors for the densification of ceramic powder. Improved properties result from the small grain sizes and high interfacial surface areas. Nanosized powders increasing sinterability at lower temperatures with smaller residual pores and grain sizes.

The state of agglomeration is particularly important in ceramic powders synthesized by wet chemical means. Agglomerates can enhance flow characteristics of nano-powders, they usually result in poor packing and incomplete densification. It is generally accepted that soft agglomerates, which disintegrate during green forming of compacts, do not impede densification.

Recently, considerable efforts has been expended in developing low-temperature routes for the chemical synthesis of ultrafine ceramic powders.

A lot of processes exist to obtain the nano-size  $Y_2O_3$  doped tetragonal Zirconia powders with precision stoichiometry. But only some processes allow to operate the particle size, its morphology, and, as a result, its feature sinterability. One of such processes is Oxalate processe. It is one of the most easy, and low expensive (cost effective) method.

Nearly monodisperse zirconia, and yttria-stabilized zirconia nano-powders were prepared by the controlled decomposition of the control synthesized zirconia and yttria oxalates.

The control synthesis of zirconia from its oxalate following by the yttria oxalate decomposition and yttria synthesis on the surface of just now synthesized zirconia nano-particles was realized.

Dependents of the particle size and morphology of zirconia oxalate on its processing parameters were investigate. The methodology of the final oxalate properties operating was elaborate.

Finally the methodology of operating by the parameters of the yttria stabilized nano-size zirconia powders was produce. This methodology allowed obtaining of the nano-powders with needful size (nearly monodispersed) and morphology, suitable for subsequent processing.

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### CERAMIC MATERIAL ON BASE OF ALKALINE SILICATES

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Ceramic material on the base of alkaline silicates perspective as modern insulating material, for a winterizing of wooden, brick and concrete sewer, as well as for getting defensive-decorative covering. Advantage of such material is their base - an inorganic composition, so they firm against different microorganisms, do not select bad materials in the process of usages of. On the other hand raw material for getting these material serves wide-spread source - quartz sand and soda that ensures an ecological clean production, helps to reduce a prime cost of product and brings about broad using these material in practice. In work a speech a problem of getting heat an insulation, defensive-decorative material on the base of alkaline silicates possessing high mechanical toughness and chemical stability.

Technological scheme of getting composition of material on the fluid glass base, includes the following stages: fluid glass syntheses; the reception of granules or defensive-decorative covering; thermal processing - ballooning material. Fluid glass Syntheses with the different silicate by the module conducted an alkaline way from amorphous silica. Installed that phase composition and pulverized particles  $\text{SiO}_2$  influence upon the dissolution its in alkalis. Reception of granules conducted with additives, enlarging mechanical toughness -  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{ZnO}$  or in dissolve  $\text{CaCl}_2$ . As fillers used powder pulverized porcelain,  $\text{ZrO}_2$ , tremolit  $2\text{CaO} \cdot 5\text{MgO} \cdot 8\text{SiO}_2$ , diopsid  $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ . Ballooning conducted at the temperature 573-673K. Defensive-decorative covering received on different carriers. Inorganic pigments used For getting the painted covering.

Studied physicist-chemical characteristics of tinning material depending on structures of filler. Installed compositions of pigments and fillers adding high mechanical toughness and chemical stability and required heat an insulation characteristics of silicate material. For tinned material are determined optimum correlations of source components.

THE RECEPTION POROUS FILTERING CERAMICS ON THE  
BASE OF DEPARTURES OF EARNING ONE'S LIVING PRODUCTION.

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The paper of the technology of reception of porous nontight ceramic materials is considered, which basic components are wastes of a line of industrial manufactures of Republic Belarus by.

The technological process includes the following operations: scattering of powders, preparation the mix, pressing and sintering. Scattering allows to allocate necessary fractions of powders (50÷1000 microns), which provide reception of demanded properties of made materials. In a mixed powder is filled in plastic fixer, and then the mix is dried for removal of a solvent and is sifted through a sieve. Samples pressing with pressure 5÷10 MPa. Formed products were exposed to sintering of the furnace under temperatures 1100÷1180 °C.

For revealing element structure and structure of samples the quantitative stereologic analysis on the automatic analyzer of the image, Mini Majiskan " under the program, " Geniay-26 " was carried out microrentgenstructure the analysis. It has been established, that basic elements used wastes are SiO<sub>2</sub>, CaO and FeO. Calculations of porosity and size porous was carried out from photos received through scanning electronic microscope, Nanolab 7 " with increase (0,25...1)·10<sup>3</sup>. The processing of results of the analysis of the image was carried out under the program, " Results ".

The received products are characterized by good mechanical durability, wear resistance and chemical stability in alkaline environments.

The considered technology allows to receive multifunctional filtering elements with high technical and economic parameters.



## THE OPTICAL COMPOSITES FORMED BY THE SOL-GEL METHOD

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Cu- and Cu/Ce-containing glass-composites on the base of silica can be used as optical functional materials and thermostable coloured filters [1]. Sol-gel process for composites synthesis is preferable because its low temperatures and high efficiency.

The copper containing silica composites were prepared by modified sol-gel process [2], including the preparation of Cu-doped silica gel-glass and treatment the latter in the hydrogen atmosphere.

The flowchart of modified sol-gel process incorporates the following stages: TEOS hydrolysis and polycondensation in the system  $\text{Si}(\text{OC}_2\text{H}_5)_4$  -  $\text{H}_2\text{O}$  -  $\text{HCl}$  with mole ration 1 : 16 : 0.01, addition the fumed silica (aerosil A-300) into the sol as filler, ultrasonic dispergation and centrifugal separation from agglomerates and dust particules. Then the polydispersed sol was neutralized up to  $\text{pH}=6,5$  by ammonia solution and was cast into fluoroplastic moulds to prepare the solid gels shaped as disks. The wet gels were formed during 20-30 min in sealed containers; then the containers were opened and the gels were washed by bidistilled water. The resulting gels were dried slouly at  $60\text{-}80^\circ\text{C}$  in the period 7-14 days in air and presintered at  $600^\circ\text{C}$  in 2 hours. After thermotreatment the xerogels were impregnated by water solutions of  $\text{CuCl}_2$  and mixture of Cu- and Ce-chlorides. So prepared impregnated gels were dried and sintered in air at the temperature  $1200^\circ\text{C}$  followed by the treatment in  $\text{H}_2$  flow at  $1000^\circ\text{C}$  in the period of 2 hours.

UV - VIS - IR - spectroscopy were used for characterisation of optical properties of glasses and Cu-, Cu/Ce-composites. The composites, containing 0,5 - 1,0 mass.% of doping elements posseses by optical transparence and ruby colour. XRD-investigations shows absence of crystalline phases in the amorphous silica glass matrix.

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# PTCR MATERIALS FOR LOW-TEMPERATURE THERMOSTATIC HEATERS

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Some electronic devices (e.g. sensors) often operate under the atmospheric conditions when significant fluctuations of the temperature ( $-40...+40^{\circ}\text{C}$ ) occur; in this case their characteristics may be essentially changed. The utilization of temperature stabilized heaters based on PTCR ceramics seems to be expedient with the view of the enhancement of their performance characteristics which does not require electronic circuits for the temperature stabilization.

Therefore, the aim of this work was the synthesis, and investigation of the properties, of PTCR materials based on the barium titanate with the stabilization temperature of 20 to  $100^{\circ}\text{C}$ .

The semiconducting materials based on the barium titanate with

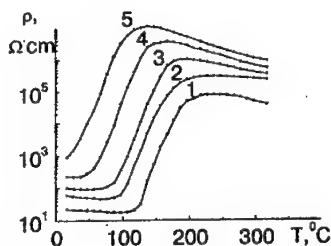


Figure. Temperature dependencies of the resistivity in  $(\text{Ba}_{0.996}\text{Y}_{0.004})(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ ,  $x = 0(1); 0,03(2); 0,05(3); 0,1(4); 0,15(5)$

partially substituted calcium and strontium for barium, zirconium and tin for titanium, were investigated. The data on the influence of aliovalent substitution in cation sublattices on the temperature behavior of PTCR elements (see figure), in particular, on their stabilization temperature have been obtained. The correlation between the microstructure of the

ceramics together with the content of alio- and isovalent dopants, and the stability of behavioral characteristics against the voltage applied have been estimated.

The field of semiconducting properties has been determined subject to the content of different dopants. The peculiarities observed were explained in terms of thermodynamic analysis of the formation processes of the ferroelectric-semiconductors taking into account isostructural replacements in the cation sublattices. The data obtained allow the goal-directed choice of the materials to be used in low-temperature heaters for the electronic devices.

# **ELECTRICAL PROPERTIES OF THICK MICROCOMPOSITE FILMS ON THE BASIS OF HIGH-DISPERSED POWDERS**



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Composite materials on the basis of powders obtained from solid solutions  $\text{Sn}_{1-x}\text{Sb}_x\text{O}_2$  are widely applied to manufacturing high-resistance thick-film resistors and gas sensors. As adopted, such compositions are prepared by mechanical mixing powders of a current-conducting material and glass in an organic binder. The paste obtained by a method of screen printing is put on a ceramic substrate to be a subject to heat treatment. Consequently, in volume of a composition, it is impossible to avoid structural trace elements and to ensure the microuniformity of the composition and structure of the films. Besides, in this case it is impossible to control the thickness of glass interlayers between conducting particles. In the present work the very assumption is made that it is possible to eliminate the defects by applying the powder of a conducting material, on the particles of which a thin film of a glass material is laid beforehand. The purpose of the present work was the development of a method of application of glass with adjustable thickness on nanofilm particles  $\text{Sn}_{0.9}\text{Sb}_{0.1}\text{O}_2$  and the investigation of its influence on electrical properties of thick-film resistors.

The powders  $\text{Sn}_{0.9}\text{Sb}_{0.1}\text{O}_2$  were obtained through calcination of coprecipitated tin and antimony hydroxides. Further on thin layers of aluminium, barium and boron compounds from water solutions were precipitated on the particles of the powder. Under heat treatment there was their decomposition and formation of amorphous glass occurred in the system  $\text{BaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ . The work dealt with investigation of electrical properties of the thick films made of these powders and also the compositions containing additional small amount of amorphous or crystallized glass.

It was confirmed that the presence of a thin glass film on the surfaces of conducting particles results in 3 - 10 fold increase of sheet resistance of composite layers, depending on its thickness. The resistance of a composition containing a powder without a coating changes during repeated heat treatments. The resistance of layers containing particles of a conductor with a coating actually remains constant. The temperature - resistance dependencies of resistive compositions were investigated and activation energy of electroconductivity was calculated.

### VANADIUM OXIDE COMPOUNDS FOR THE CATHODES OF LITHIUM ACCUMULATORS

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At cycling in lithium accumulators  $V_2O_5$ -based cathodes gradually lose discharge capacity as a result of structural reorganization. For the improvement of  $V_2O_5$  discharge characteristics two methods of its modification: electrolysis and thermal synthesis with glass - formation modifiers were used.

Amorphous ( $a\text{-}V_2O_5$ ), one of the produced modifications, is a product of high thermal synthesis with subsequent rapid cooling of melt. As glass formers,  $GeO_2$ ,  $TeO_2$ ,  $B_2O_3$ ,  $Bi_2O_3$  and the mixtures of  $GeO_2$ ,  $TeO_2$  or  $P_2O_5$  with  $MoO_3$  or  $WO_3$  oxides were used. With 10-15 mol.% content of modifier, the amorphous compositions of  $V_2O_5$  with  $GeO_2$  or  $TeO_2$  have been produced. The compositions, where amorphous phase coexists with microcrystalline one, have been synthesized as well. The synthesized glasses have been studied by the methods of X-ray diffraction, IR absorption spectroscopy, thermal analysis and electrochemical methods. The comparison of specific discharged characteristics of the synthesized amorphous  $V_2O_5$  compositions with those of crystalline  $V_2O_5$  ( $c\text{-}V_2O_5$ ) has been carried out. The amorphous compositions have higher energy content as compared with those with  $c\text{-}V_2O_5$ : the open circuit voltage of  $a\text{-}V_2O_5$  is higher than with  $c\text{-}V_2O_5$ . The cycling efficiency of  $a\text{-}V_2O_5$  in electrolyte: PC+DME+1M.LiClO<sub>4</sub> (PC-propylene carbonate, DME - dimethoxyethane) exceeds significantly the efficiency obtained for  $c\text{-}V_2O_5$ . Discharge capacity loss of the amorphous contents during the tenth cycle does not exceed 15%, whereas for crystalline ones it reaches 50 and more percents.

Electrochemical modification ( $e\text{-}V_2O_5$ ) was synthesized anodically from vanadyl sulfate electrolyte followed by thermal treatment. Electrolysis in  $Na^+$ -containing vanadyl sulfate electrolyte was also carried out. In this case sodium vanadium oxide bronzes of monoclinic singony have become the final products of the synthesis, which are promising cathode materials for lithium accumulators. Initial specific discharge capacity of electrolytic bronze  $\beta\text{-}Na_{0.33}V_2O_5$  reaches 320 Ah/kg at discharging by the current of 100  $\mu A/cm^2$ . Bronze  $\beta\text{-}Na_{0.33}V_2O_5$  is efficiently cycled over the range of 3.7 - 2.4 V.

THE STRENGTH AND CRACK RESISTANCE OF CERAMICS AND  
COMPOSITES WITH CERAMIC MATRIX AT THE SMALL SURFACE  
DEFECTS PRESENCE

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Strength characteristics of structural ceramics and composites with ceramic matrix at static and cyclic loading in main is determined by its crack resistance. Crack resistance depends on the properties of material and from residual stresses. The main interest presents the behavior of small cracks as the structures with big cracks existence is few probable.

The investigation of strength and crack resistance of ceramics and composites in temperature interval 20-1600 C was executed. The  $\text{Si}_3\text{N}_4$  and SiC-base ceramics with additives  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ , TiN,  $\text{TiB}_2$ , AlN and the composite with  $\text{Si}_3\text{N}_4$ - $\text{Y}_2\text{O}_3$ -matrix and SiC-whiskers were used. The composite with matrix and fibers SiC was used also.

The strength was determined by three point bending method. Fracture toughness was determined by method of sample with macro notch bending, indentation method and bend of sample with indentation crack method. The cracks growth rate at the static and cyclic loading was measured. The theoretical and experimental analysis of the residual stresses influence on destruction processes was executed.

It is shown, that the fracture toughness, which is determine by bend of sample with macro notch method, is close to values, received by indentation method. Often however, it considerably surpasses the significance's of fracture toughness, which received by bend of sample with indentation cracks.

At the cyclic bend the growth of indentation cracks happens by jumps of 0.01-0.1 mm length. The average rate of crack growth is practically independence on its length. At static bend at load, which is equal to maximal load of cycle, the growth of indentation cracks is not marked.

The expressions, which described the influence of surface residual stresses and residual stresses which arise at indentation on destruction characteristic of brittle materials, were received.

**MAGNETORESISTIVE CERAMIC COMPOSITES  
ON A BASIS OF MANGANESE-LANTHANUM OXIDES  
(TECHNOLOGY, STRUCTURE, PROPERTIES)**

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Manganese-lanthanum oxides with perovskite structure concern to the most perspective materials of modern technique due to a huge magnetoresistance.

That last years a heightened interest exhibit to making nano-, meso- and macrostructural non-uniform composites. In this article the results of the examinations carried out with the purpose of searching of new high-performance magnetoresistive materials, optimization of their composition and clearing up of a nature of non-uniform composites with searching of ways of improving of their properties are represented. The charging, synthesis, pressing and baking of products are the technological basis of these ceramic samples.

Manganese-lanthanum-barium perovskites  $\text{La}_{0.7}\text{Ba}_{0.3-x}\text{Sn}_x\text{MnO}_3$  ( $0 \leq x \leq 0.3$ ) obtained by optimised technology were investigated with using X-ray, NMR ( $^{55}\text{Mn}$ ,  $^{139}\text{La}$ ), magnetic and electrical methods. According to X-ray diffraction examinations, the doping leads to multi-phase state of samples, which alongside with basic magnetoresistive rhombohedrically distorted phase  $\text{La}_{0.7-x}\text{Ba}_{0.3-x}\text{MnO}_3$  ( $R\bar{3}c$ ) contained  $\text{La}_2\text{Sn}_2\text{O}_7$  with spinel structure ( $\text{Fd}3m$ ). By NMR-examinations on  $^{55}\text{Mn}$  set multi-valent ions of manganese ( $\text{Mn}^{3+}$ ,  $\text{Mn}^{4+}$  in A-positions) are in a high-frequency electronic exchange and their widened spectrum (300-430 MHz) became complicated at the x change.  $^{139}\text{La}$  NMR-spectrum is displaced and unsymmetrically widened (10-30 MHz) in the side of low frequencies at the x magnification. It, on ours opinion, is bound to a crystallographic and magnetic nonequivalence of  $\text{La}^{3+}$  environments (in A-positions) owing to a presence in B-positions not only multi-valent manganese ions, but also cationic vacancies. The real structure at that contain mesoscopic nano-structural inhomogeneities of cluster type.

Positive is that the magnetoresistance ( $\Delta R/R_0$ ,  $H=5$  kOe) of these hetero-phase-nonuniform ceramic samples is increased in 3 times at x increase.

**CERAMIC SEMICONDUCTING Cu, Ni, Co, Mn BASED  
SPINEL COMPOSITES FOR NTC THERMISTORS:  
STATE OF THE PROBLEM AND APPLICATION PROSPECTS**

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The peculiarities of Cu,Ni,Co,Mn based spinel materials formation in the  $\text{Cu}_x\text{Ni}_{1-x-y}\text{Co}_y\text{Mn}_{2-y}\text{O}_4$  ( $0,1 \leq x \leq 0,8$ ;  $0,1 \leq y \leq 0,9-x$ ) system under different sintering conditions have been studied by the methods of X-ray diffraction, optical microscopy, electron-sonde microanalysis and electrical measurements. Traditional ceramic processing techniques for samples preparation in the form of disk have been used: obtaining of the metal oxide powders, milling and blending with binder, sintering, electrical contacts forming.

Structure-property relations in ceramic semiconducting composites (CSC), obtained at three different sintering temperatures ( $T_s$ ) regimes: I - low temperature regime ( $T_s = 0,5-0,75$  of the spinel solid solution melting temperature  $T_m$ ); II - intermediate temperature regime ( $T_s = 0,75-0,85T_m$ ); III - high temperature regime ( $T_s \geq 0,85T_m$ ), are discussed.

Two groups of investigated CSC samples with different character of electrical conductivity dependencies on  $T_s$  can be divided. The materials of the first group are characterized by monotonic  $\sigma(T_s)$  dependence, the other CSC reveal extremums at the  $\sigma(T_s)$  relationships.

The origin of these effects is discussed in the framework of the model of thermoinduced cations rearrangement in octahedral and tetrahedral spinel sites.

It has been found that at the above mentioned conditions of the sintering regime II the continuous series of solid solutions with cubic spinel structure in  $\text{Cu}_x\text{Ni}_{1-x-y}\text{Co}_y\text{Mn}_{2-y}\text{O}_4$  system are formed. Various electrical parameters of these single-phase semiconducting materials show that they are quite optimum for thermistors application.

The mathematical models of the electrical conductivity at 298 K  $\sigma_{298}$ , preexponential factor  $\sigma_0$ , activation energy  $\Delta E_{290-340}$  and lattice constant as a function of chemical composition for single phase spinel-based CSC in studied system have been constructed using experimental-statistical methods.

# GAS SENSITIVITY CERAMICS OF CUPER OXIDES

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The physical properties high-temperature superconducting ceramics on the basis of the cuprate oxides are much influenced by the gas environment. It allows to apply of such ceramics in the devices sensitive to gases. In this work materials as YBaCuO and related non-superconducting phase were investigated which at the moment have the best opportunities for practical application. Oxide cuprate ceramics are characterized by open system pores. The majority pores have the sizes not less 1000Å, they are well connected among themselves and penetrate whole volume of ceramics. The ease of the gas exchange is defined in the small length of diffusion of gas atoms to inside of the grain from a surface nearest of pore.

In the work the non-superconducting cuprate phases of CuO, BaCuO<sub>2</sub>, Y<sub>2</sub>BaCuO<sub>5</sub> type which are the nearest thermodynamically surrounding of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (x = 0.1-0.7) superconducting phase have been investigated. CuO, BaCuO<sub>2</sub> and Y<sub>2</sub>BaCuO<sub>5</sub> ceramics samples are prepared using the standard technology: the powder mixture of initial oxides of stoichiometric composition after homogenisation were pressed into disks and annealed. The disk diameter and thickness are 10 mm and 2 mm accordingly. The annealing was in air between 950°C and 1000°C for 5-8 hours. After synthesis the samples were cooled to the room temperature with the velocity near 5-10°C/min. The samples are characterized by complete combination of the grains with the average size of crystallites of 0.3 μm that is near to the size of initial powder particles.

The results of experimental researches of the gas sensitivity find an explanation within the framework of the electronic theory catalytic, establishing connection between sorption and catalytic properties of the surface and electrical characteristics of ceramics. The change of electrophysical parameters is determined by donor-acceptor character of the electronic exchange between the adsorption phase and crystal lattice of the oxide. The majority cuprate oxides is characterized by the p-type of conductivity, that causes its reduction at the chemisorption of donor molecules such as (acetone, ethanol, diethyl ether, oxide of carbon CO). Absorption of the acceptor molecules (oxygen, chlorine, oxide of nitrogen NO<sub>2</sub>) causes increase of the conductivity such ceramics. The selectivity depends on activation energy (Ea) of the chemisorption gas, as the concentration of adsorption molecules is  $n = \exp(-Ea/kT)$  determines concentration additional electrons in the crystal lattice. The Fermi energy position determines correlation between the influence of the external factors (electrical field, illumination, implantation) and speed catalytic of reactions on a surface cuprate oxides.



**THE NEW ECONOMIC MATERIAL FOR POWER SOURCES  
ON A BASIS OF  $\text{MnO}_2$  (WITH A WEAK ADHESION)  
FROM FLUORINE-CONTAINING ELECTROLYTES**

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The Advantages of material for power sources on a basis of  $\text{MnO}_2$  which recieved from fluorine-containing electrolytes sources are discussed. It is known that structure and the properties of manganese dioxide depend on a method of its obtaining. The authors had investigated different samples: (I)- from fluoride and (II) - from sulfate containing electrolytes. The chemical composition and crystal structure (DRON-3, Mo  $K_\alpha$ ) of these samples was essentially differ. The main phase in the samples is a  $\gamma$ -modification  $\text{MnO}_2$  (Pnam). That is confirmed by transmission electron microscopy method (JEM 100-CX). Sample (I) contained  $\alpha$ - $\text{MnO}_2$  as impurity phase (I4/m) also. It was established by a XPS method (Kratus Analytical,  $\text{MgK}\alpha$ ; operator A.I. Senkevich), that electronic structure for the given materials also quite different. The Valency Band and  $2p_{1/2, 3/2}$  - electron spectrum of sample (I) have some details due to a Charge Transfer Complexes (CTC) of d-metals, (wich are the defects of chemical nature in such compounds, stabilized by OH-groups). These data agreed with results received by EPR-method too. The main advantages of electrolytic manganese dioxide, which received from fluoride-containing electrolytes are: 1/-weak adhesion  $\text{MnO}_2$ (I) to a substrate in comparison with (II)(this electrolytic manganese dioxide is more cheapest because in the technological scheme of its manufacture the stage of separation product from an electrode is absent); 2/-the crystalline structure with many of defects and special electronic structure, (which result in more higher catalytic activity); 3/-the mass transfer process at the electroreduction of such samples is facilitated. These and many of other features determine the unique electrical characteristics  $\text{MnO}_2$  (I) as the bases component of the cathode matherial for a chemical power sources.

## FORMATION OF COMPOSITE POWDERS AND CERAMICS BASED ON $\alpha$ -, $\beta$ -SiC, AND CHROMIUM CARBIDES

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The synthesis of ultrafine composite powders based on nonmetallic compounds exhibiting high hardness, strength, chemical and temperature resistance, etc. extends substantially the fields of application of single-phase materials that have already been studied well. In recent years attention has been focussed on the SiC-based composite ceramics with additions of titanium, chromium, and molybdenum carbides, etc. The problem of preparation of homogeneous mixtures of starting powders, in this connection, has acquired great importance. The application of the sol-gel method at the stage of preparation of composite powders proves to be preferred.

In this work the process of formation of the disperse  $\alpha$ -SiC or  $\beta$ -SiC system with additives of chromium carbides obtained from soluble chromium salts and carbohydrates within the framework of the carbothermal reduction of  $\text{Cr}_2\text{O}_3$  is considered.

It has been found that in the course of high-temperature treatment of the mixtures in vacuum in the temperature range 600-1600°C the processes of carbothermal reduction of  $\text{Cr}_2\text{O}_3$  proceed with the formation of  $\text{Cr}_7\text{C}_3$  and further  $\text{Cr}_3\text{C}_2$ . The content of chromium carbides is specified by the  $\text{Cr}_2\text{O}_3/\text{C}$  ratio and by the temperature-time conditions of treatment. As the carbon content in the starting mixtures increases, after heat treatment at 1600°C the  $\text{Cr}_3\text{C}_2/\text{Cr}_7\text{C}_3$  ratio and the lattice parameter  $a$  for all considered carbides increase, and diffraction lines broaden. In the samples based on  $\alpha$ -SiC the content of chromium carbides is higher than that in the samples based on  $\beta$ -SiC. Chromium carbides are uniformly localized in the interaggregate space which consists of silicon carbide.

Composite powders synthesized at 1600°C were compacted under a pressure of 5 Gpa and at a temperature of 1800°C. In this case, the refinement of  $\alpha$ -SiC crystals as well as the  $\alpha$ -SiC  $\rightarrow$   $\beta$ -SiC transformation, and the transition of  $\text{Cr}_3\text{C}_2$  into  $\text{Cr}_7\text{C}_3$  took place. The distortion of lattices of silicon and chromium carbides were detected.

# XPS AND XES STUDIES OF THE ELECTRONIC STRUCTURE OF THE $\epsilon$ AND $\zeta$ PHASES IN THE Ta-C SYSTEM

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X-ray photoelectron (XPS) and emission (XES) spectroscopy methods have been used to study the electronic structure of rhombohedral  $\zeta$ -Ta<sub>4</sub>C<sub>3</sub> and  $\epsilon$ -Ta<sub>3</sub>C<sub>2</sub> phases. For comparison, the electronic structure of cubic TaC<sub>x</sub> and hexagonal Ta<sub>2</sub>C<sub>y</sub> ( $y=2x$ ) carbides over the range  $0.36 \leq x \leq 0.98$  have also been studied. The XES bands in all the compounds studied have been compared in a single energy scale with the XPS valence-band spectra. The XPS core-level binding energies (BE's) and valence-band structures for TaC<sub>x</sub> have been determined. In the layered subcarbides  $\zeta$ -Ta<sub>4</sub>C<sub>3</sub> and  $\epsilon$ -Ta<sub>3</sub>C<sub>2</sub> the formation of new (shortened) M-M bonds between the tantalum atoms neighbouring the {111} plane of the carbon sublattice, where the C-vacancies concentrate, results in the appearance of an additional peak ( $E_{BE} \approx 2$  eV below  $E_f$ ) in the XPS valence-band spectra [1]. In the sequence TaC<sub>0.98</sub>  $\rightarrow$   $\zeta$ -Ta<sub>4</sub>C<sub>3</sub>  $\rightarrow$   $\epsilon$ -Ta<sub>3</sub>C<sub>2</sub>  $\rightarrow$  TaC<sub>0.36</sub> the XPS Ta 4f and C 2s core-level BE's and main peaks of the XPS valence-band spectra shifted toward the Fermi level by 0.5 to 0.85 eV, while the C 1s BE remained constant (within the experimental error) for all subcarbides studied [1,2]. In the mentioned sequence some shifts (0.6 to 0.9 eV) of the main maxima of the XES Ta 5d-like and C 2p-like bands toward  $E_f$  are observed. The C K $\alpha$  band half-width decreases by 0.3 eV going from cubic TaC<sub>x</sub> carbides to hexagonal Ta<sub>2</sub>C<sub>y</sub> carbides, but the C K $\alpha$  band asymmetry index increases from 0.72 in TaC<sub>0.98</sub> to about 1.75 in the carbides Ta<sub>2</sub>C<sub>y</sub>. In all tantalum subcarbides investigated the energy positions of the centers of gravity of the C 2p-like emission bands remain constant. The results of the XPS and XES studies indicate that the layered subcarbides  $\zeta$ -Ta<sub>4</sub>C<sub>3</sub> and  $\epsilon$ -Ta<sub>3</sub>C<sub>2</sub> are individual phases and are by no means a simple mixture of the cubic TaC<sub>x</sub> and hexagonal Ta<sub>2</sub>C<sub>y</sub> carbides. In all tantalum carbides studied the charge transfers from Ta atoms to C atoms, but the Ta 5d-like and C 2p-like states are strongly hybridized [1,2].

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# MECHANISM OF BORON - ALUMINIUM- CARBON CERAMICS FORMATION

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Boron-rich solid are as rule the most light and the most hard and in this plane give only a diamond and cubic boron nitride in . However, namely boron-rich solid are the least studied of well known boron containing phases. Especially a given affirmation concerns to aluminium boron-containing phases. In the present communication are firstly described experimental results related to the study by means of the differential thermal analysis method of the interaction of boron with aluminium and carbon with the purpose of light Al-B or Al-B-C ceramics obtaining and the study of it properties. Investigations were carried out on the apparatus which permits to lead the tests into a vacuum or an inert gas at the temperature up to 1800o C. Temperatures of the nucleation and the forming of borides and borocarbides at different rates of the sample heating were determined. The interaction in Al-B-C systeme both a vacuum and an inert gas starts with the lowest boride AlB12 then dodecaboride AlB12 and completes by the forming of borocarbide. The forming temperatures boron-containing phases depend from the samples heating rate and do not practically depend from the medium (vacuum or inert gas) of the reaction. The temperature of formation aluminium boron containing phases increases with diminution of the reagents Al/B ratio in a initial mixture. So, phase AlB2 the formation temperature - 750oC, phase AlB12 - 960oC and phase Al3B48C2 - 1020oC. Pirotectic decomposition of a phase AlB2 is realizing at 980oC and has not depend from initial reagents a state, which are formed a given phase. Besides it was established that the state of boron powder (crystalline and amorphous) and aluminium powder the dispersion degree influence not only on the temperature of the reaction start but and on the texture of the obtained powder-like the product. Attestation the reaction synthesised products was performed using chemical, X-ray and crystalloptical as well as by dint of electron microscopy and optical spectroscopy. The mechanism of creation and growth of aluminium boron-containing phases is proposed, which suppouses not boronizing metal but aluminiumizing boron. Limited stage in the given mechanism of boron aluminiumizing is the stage of aluminium intrusion into boron primary lattice. Powdery but not sintered the form of obtained from simple substances aluminium borides and borocarbides is connected that the reaction heating effect their formation is spent not only on temperature increasing of reactionary system but and on aluminium evaporation.

# CERAMIC MATERIALS BASED ON BARIUM-LANTHANIDE TITANATES FOR THE APPLICATIONS IN MW TECHNIQUE

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At present, microwave (MW) materials with enhanced value of dielectric permittivity ( $\epsilon \approx 70-100$ ), low dielectric losses denoted by  $\tan \delta$  value, together with the high temperature stability of electro-physical properties find wider and wider applications in the modern communication equipment. The barium- lanthanide titanates  $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ , which form the solid solubility region at limited  $x$  values, are of a great current interest as a basis for developing these materials. The number of questions concerning the nature of electro-physical properties of barium-lanthanide titanates remain unexplored which make difficult the utilization of the materials based on them in MW engineering.

This work represents the results of studying the formation conditions of barium- lanthanide titanates when synthesized them by the conventional ceramic technique. It has been shown the initial formation of end-member phases corresponded to the highest  $x$  values in the system of solid solutions  $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$ , where  $\text{Ln} = \text{Nd}$ ,  $\text{Sm}$  followed then by  $\text{Ba}_{6-x}\text{Ln}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$  ss formation due to the interaction between these «low temperature» end-member phases and barium titanate ( $\text{BaTiO}_3$ ).

The possibility has been shown in the controlling temperature stability of the materials due to the partial isovalent substitution of calcium and lead ions for barium ions in the systems  $(\text{Ba}_{1-y}\text{Ca}_y)_{6-x}\text{Sm}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$  and  $(\text{Ba}_{1-z}\text{Pb}_z)_{6-x}\text{Nd}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$  respectively. The temperature stabilization in  $\text{Sm}$ - containing samples was explained to be originated in the presence of structural phase transitions, and implemented on account of the temperature shift of these transitions against partial calcium substitution for barium. In neodymium- containing systems the temperature stable materials have been developed over the wide range of the lead concentration, which were distinguished by high level of electro- physical properties together with high dielectric constant controllable within the confines of 80 to 100.

## GLASS - ABRASIVE COMPOSITES FOR INSTRUMENTAL USE

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Low-temperature led - containing glasses are being used successfully as the bonds in abrasive and diamond tools. Melts of glasses in PbO - ZnO - B<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> and PbO - ZnO - B<sub>2</sub>O<sub>3</sub>, PbO - B<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> and PbO - B<sub>2</sub>O<sub>3</sub> demonstrate satisfactory wetting of diamond and CBN within temperature interval 430 - 520 °C. The process of melting determines the lower temperature limit of wetting, the process of crystallization determines the upper one.

High strength of abrasive composites is caused by good adhesion between the melt of glass and the surface of superhard materials (158 - 320 mJ/m<sup>2</sup> in the temperature interval 410 - 490 °C). Such effect is connected with chemical interactions at the interface.

According to IR-spectroscopy data, diamond begins to react intensively with glass melts at 800 °C, CBN - at 500 °C.

One of the important criteria for the choice of bonding components and optimization of technological parameters is the strength of fastening of the diamond grain. Maximum of fastening strength for diamond (114 MPa) and CBN (150 MPa) demonstrates the glass in PbO - B<sub>2</sub>O<sub>3</sub> system. PbO - ZnO - B<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> glasses have high crystallization ability. The fastening of diamond grains increases with the growth of crystalline phase content.

# INFLUENCE of ORIENTATION of FIBRES ON DURABILITY of COMPOSITES $\text{LaB}_6\text{-MeB}_2$ .

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Composite materials  $\text{LaB}_6\text{-MeB}_2$  (where  $\text{MeB}_2\text{-TiB}_2, \text{ZrB}_2, \text{HfB}_2$ ) received by directed crystallization of eutectic liquids in conditions zone melting of powder preparations with a driven solvent of impurity with speeds of a movement of a zone liquid 2,8; 3,8; 4,8; 5,2 mm / mines. (110) matrix phases from  $\text{LaB}_6$  were cut in a longitudinal direction on a plane.

By methods quantitative metalography were defined the size and quantity armature diboride of inclusions. Is shown, that the size of inclusions can effective be adjusted by intensity of hashing of liquid.

On samples with the approximately identical size of inclusions, but grown with various speeds, of a melting zone, orientation of diboride fibres and subgrains of a matrix phase is studied.

X-ray-structure analysis on the diffractometric complex, which uses four district equatorial geometry of shooting with independent rotation of a sample and by moving of the detector is established, that with increase of crystallization speed of a composite is increased both quantity, and orientation angle of fibres concerning a matrix and fibres one to other.

The increase of durability of composites in process of growth of crystallization speed is explained by change of structure of a composite from reinforced in one direction with  $V < 2,8$  mm / mines. to volumetric – reinforced with large speeds of cultivation.

# INFLUENCE OF BORON ADDS FOR SINTERING OF TRANSITION METAL BORIDES.

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It is studied the densification of the green bodies with porosity of 45-50% from the powder blend of  $\text{MeB}_2$  ( $\text{TiB}_2$ ,  $\text{ZrB}_2$ ,  $\text{HfB}_2$ ) and amorphous boron of 0, 1, 3, 5, 10 and 20 mas.% at the sintering in the conditions of the induction heating with speed of 300-350 grad/min in the field of the large temperature gradient (1000 grad/sm).

It is shown, that concentration dependence of shrinkage has nonmonotonous character. Boron adds up to 5 mas.% activate of the green body densification at  $T=1570-1650$  C. The shrinkage increases in the row of  $\text{TiB}_2$ - $\text{ZrB}_2$ - $\text{HfB}_2$ , and from the data of x-ray phases quantitative microscopic and durometric analysis, specimens consist of tree phases:  $\text{MeB}$ ,  $\text{MeB}_2$  and B. Increasing of the sintering temperature up to 1750-1800 C is resulted to increasing shrinkage in 3-4 times, and in specimens with more then 3 mas.% of boron is found only two phases ( $\text{MeB}_2$  and B) for  $\text{TiB}_2$ -B and  $\text{HfB}_2$ -B systems and tree phases ( $\text{MeB}_2$ ,  $\text{MeB}_{12}$  and B) for the  $\text{ZrB}_2$ -B system.

It is shown, that the lattice period of diborides increases at increasing of quantity of boron and nonmonotonously changes with increasing of the sintering temperature, that results of existence of wide gomogenous region of diboride phases, which in condition diagram expands with increasing of the sintering temperature, and then narrowing near melting temperatures of diborides. It is defined, that in  $\text{TiB}_2$  dissolve up to 3 mas.% of boron at  $T=1700-1800$  C.

By fractographic investigations of sintering specimen breaks are shown, that boron adds result to smoothing of the particle isthmus surface and activate of the local nongomogenous densification, which at boron adds of more then 5 mas.% decrease of volume shrinkage of specimens and result to form of connected large porous channels in the sintering material.



# MANUFACTURE, PROPERTIES AND OUTLOOK OF USING OF COMPOSITES WITH THE SILICATE-PHOSPHATE MATRIX

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The conditions of manufacturing of pore ceramics the basic of which is biological hydroxiapatite (BHAp) and oxide of silicon are elaborated.

BHAp was made in composition of mixture as crushing native bones of animals and as ash [1,2]. Some oxide of natrium and oxide of boron are also in composition with the purpose of reducing of the temperature of softening.

It was used the method of two-stage coagulation at  $T > 1000^{\circ}\text{C}$  and  $T < 1000^{\circ}\text{C}$ .

The compound of obtained samples was controlled by the methods of chemical and X-ray phase analysis. The common contents of carbon in composition of a number of composites were achieved by the method of coagulation in the flow of refined oxygen at  $T = 1300^{\circ}\text{C}$  and was controlled with the half-quantity method of IR-spectroscopy.

It was established that in the specimens coagulated at  $T > 1000^{\circ}\text{C}$  the quantity of carbon nearly in twice exceed the same in composition of more low-temperature composites at equal quantity of BHAp in starting mixture and in same range of particles before secondary coagulation. Besides the maximal quantity of carbon in obtained composites with maximal contents of native BHAp didn't exceed 3 % mass that is significant for the mineral of bones on mammals.

It was established that it is possible to change the porosity of samples in the limit of 11-60 vol.%. Volume density ( $\text{g}/\text{cm}^3$ ) of samples, speed of dissolving in the water and synthetic physiological solution, the compressive strength, the peculiarity of optical absorption in interval of spectrum 0.2-25  $\mu$  were determined.

The perspectives of using of prepared composites as bioactive materials in orthopady were examined.

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**FIBER-REINFORCED ENGINEERING  
GLASS-CERAMIC COMPOSITES:  
TECHNOLOGY PECULIARITIES, STRUCTURE EXAMINATION,  
MAIN PROPERTIES AND APPLICATION PROSPECTS**

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The authors summarize their many-years researches in the area of development of reinforced glass-ceramics for engineering materials that will be investigated under liquid and gas corrosive media (e.g. chlorine atmosphere, sea water) and high temperature gas flows of up to 1100 °C.

Apart of effects involved during the reinforcing with brittle fibers, flexible metallic fibers made of stainless steel or nickel-chromium, when used as reinforcement, will enhance the strain effect and fracture work due to the contribution of these into the plastic deformation of the fibers. Thus, an opportunity is provided to have products with a sufficient level of heat resistance at the matrix fragmentation under loading, and retention of an integrity for the fragmentized product at a satisfactory level of residual strength due to the fiber effect.

The reinforcement of glass-ceramics with a knitted net of metallic fibers can be considered as an approach to the development of a 3-D frame.

The report describes peculiarity of the technology, structural analysis of the fracture process, and main properties of continuous metal fiber reinforced ceramics.

The engineering materials are planned to be used in airspace, chemical, vehicle construction industries and other areas as heat resistance and impact resistance materials.

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**INFLUENCE OF STRUCTURAL AND PHASE CONDITIONS OF  
INITIAL COMPONENTS TO FORMATION OF INTERMEDIATE  
PHASES AT SYNTHESIS OF CORDIERITE**

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The purpose of the present work - to investigate a sequence of phase transformations in multicomponent cordierite mixtures, derivated by oxides Mg, Al, Si in the ratio 2: 2: 5, their synthetic and mineral compounds have a various dispersibility, structure and phase composition. The initial mixtures of powders with a size of grains 2-3 microns consist from alumomagnesium spinel and amorphous silica, enstatite, silica and aluminum oxide, mullite, magnesium oxide and silica, kaolin, silica and magnesium oxide, kaolin, talc and pyrophyllite. The various activation modes of natural minerals, including acid handling ( $H_2SO_4$ ,  $HNO_3$ , HF) and handling by explosion are used.

Datas on synthetic cordierite properties and possible paths of a drop of synthesis temperatures and extension of a cordierite ceramics sintering temperature interval are studied and related.

### METHOD OF SYNTHESIS OF BORON CARBIDE FIBERS

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New method of synthesis of boron carbide fibers by means of impregnation precursory fibers with boron containing solutions and their thermal treatment is developed. The method is useful for manufacturing continuous fibers as well as various fiber combined structures, for example felts, nets, fabrics, knitwear etc. Hydrated cellulose was used as precursed material. Water solutions of boric acid with various additions were of the boron source. It turned out that only by using the hot solution with temperature 70-100 °C it was possible to carry out impregnation process successfully. Impregnation time depended on the kind of the precursor. The felt required the minimum time of impregnation while the knitwear needed the maximum time. The synthesis of the boron carbide was performed through carbon thermal reduction of boron oxide. The process includes four stages: formation of the boric anhydride, melting of the boric anhydride and spreading over the fiber surface, reduction, formation of boron carbide. The first and the second stage can be carried out without using of the protective atmosphere. Reduction of the boric anhydride and synthesis of the boron carbide are fulfilled in argon atmosphere. The effect of additional sources of free carbon on the composition of the final synthesis products was investigated. It is possible to obtain both boron carbide fibers and boron carbide coated carbon fibers by varying the ratio of initial components. Fiber structures prepared can be used, for instance, as reinforcement in composite materials.

**THE EFFECT OF THE ELECTRIC FIELD ON THE  
STRUCTURE AND THE PROPERTIES OF THE HIGH  
TEMPERATURE SUPERCONDUCTOR**

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As the result of analysis of the external electric field applied across HTSC samples it was ascertained the following.

If the electric pulse current flows through the bulk sample, three possible groups of the structural changes can occur:

- the destruction of the weakly conducting layers between the neighbouring crystallites;
- the microelectroexplosions with the resulting microcracks;
- the micromelting and the formation of the liquid microbridges.

Some of these phenomena can improve or worsen the superconductivity properties. The resulting change in the structure and the properties of HTSC ceramics is a consequence of the competition between the processes mentioned. It was observed experimentally the significant changes of the ittrium ceramics structure and the increase of the superconductivity transition temperature from 90 K up to 93 K.

In case of the external electric field without the flowing current through the sample such significant after-effects does not excite.

### STRUCTURE AND PROPERTIES OF HOT -PRESSED $W_2B_5$ - $TiB_2$ - $B_4C$ CERAMICS

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The ceramics of W - Ti - B - C system are perspective ones as the high- strength and wear- resistant materials as well as material with high absorption of ionizing radiation. In this research a study of hot- pressed ceramics fabricated using the  $W_2B_5$ -  $TiB_2$ -  $B_4C$  composite powders was carried out, the latter being synthesised by a boron- thermal reduction method.

We have investigated materials with the following component content:  $W_2B_5$ - 24-42vol.%,  $TiB_2$ - 12-45vol.%,  $B_4C$ - 12-64vol.%. The intervals of component content were determined by requests of optimization for maximum strength (fracture toughness) at given specific weight and absorption constants of  $\gamma$ -radiation and neutrons.

The materials obtained are the frame-type structure with a boron carbide matrix (at its high content) and a boride- phase binder. For a low  $B_4C$  content they are the structures of an inclusion- matrix type. The grain size depends on the preparation process and is in the range of 5- 20  $\mu m$ . The hardness of the composites obtained is in the range of 32- 35 Gpa at the strength level of 500- 600 Mpa.

Thus, the use of synthesised composite powders allows to fabricate the hot-pressed materials having the strength ~600 Mpa. What is why these composites can be included in the group of perspective ceramics with a wide enough application.

## GLASS FIBERS OF TV KINESCOPE GLASS WASTE AND POLYMER COMPOSITES MADE THEREOF

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Due to a broad spreading of computerization and high volume production of kinescopes, a need has emerged to recycle the TV kinescope glass waste. At present, a considerable amount of glass waste is accumulated comprising oxides of lead, barium, bismuth, cerium, and a wide range of rare earth metal oxides.

It was found in the result of diverse reseaches of the TV glass waste that the latter contains ingredients useful for production of continuous fibers and these can contain from 14 to 30 wt% of lead oxide, 1 to 2 wt% of rare earth elements and up to 4.5 wt% of barium oxide depending on compositions of different kinescope parts.

A technology has been developed of preparing glass fibers of the waste and lots of fibers have been manufactured dia. from 9 to 25 mkm, density of 3.3 to 4.1 g/cm<sup>3</sup>, strength of 1800 to 3000 MPa, elastic modulus of 8000 to 12000 MPa. The recycling process has no impact on the environment as lead and rare earth elements are in their bound states, besides, saves deficient raw materials and can avoid steps of silicate and glass formation in the production process.

The opportunity to use fibers as reinforcing elements for polymer composition materials with elevated protection properties under ionization radiation exposure, was examined. The composites feature a uniform ionisation absorption, a higher degree of its attenuation (1.5 time for gamma Co<sup>60</sup> radiation) relative to conventional glass laminates.

The fibers and composites developed can be used in the manufacture of portable protective filters for individual or personnel protection, when producing cases to waste storage, protective tanks for radioactive waste storage or other protective means.

# KINETIC PROPERTIES OF BORON SUBOXIDE, NITRIDE AND CARBIDE

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Solid boron compounds are advanced materials in ceramic technology thanks to formation of fusible oxides and eutectics on the surfaces of particles. Some boron compounds of carbide and nitride type are known to have most high hardness. But sometimes, when their hardness approaches the value for diamond they become brittle. This prevents to use the boron compounds more successfully.

The task is to produce superhard boron-compound-based ceramic materials having both high hardness and suitable ductility. As a rule, the more ductile and the less brittle a material is, the higher metal properties (in particular, electroconductivity) it has. The authors have investigated electrophysical properties of boron suboxide, nitride and carbide in order to understand the physical nature of formation of kinetic properties of electron transfer and to be able to make prognoses for methods for an increase of the material conductivity which may allow the ductility of the boron compounds investigated to be improved.

The investigation method chosen included experimental measurement of the temperature dependences of electroconductivity and thermoemf followed by calculation of internal electrotransfer parameters.

It has been found that in the row boron suboxide, boron nitride and boron carbide boron nitride has maximum hardness and minimum electroconductivity due to the maximum forbidden gap and minimum free carrier concentration. The authors have made conclusion that the electroconductivity may be increased, so the ductility may be improved in the boron compounds investigated and have proposed appropriate methods for this.



### Reinforcement of $\beta$ -sialon with discrete fibres.

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The present article describes influence of discrete fibres of AlN and SiC on the structure, strength and fracture toughness of composites based on  $\beta$ -sialons of two compositions ( $C_1$  and  $C_2$ ) obtained by carbothermic reducing of kaolin in nitrogen medium. The form of fibres is dissimilar if in the case of SiC the fibres are the threads with the length to diameter ratio equal to 50, than in the example of AlN they are needle-shaped prismatic crystals with the  $l/d$  ratio of about 10. The fibres were introduced by wet or dry mixing with sialon powder. The method of sandwich stacking of rolled layers of sialon and fibrous material were tested for SiC fibres.

The samples were prepared by hot pressure and their phase composition was studied by x-ray diffractometry, their microstructure - by electron-microscopic study of the fracture surface after determining of strength by three-point bending.

Table

Composition and some properties of  $\beta$ -sialons and composites reinforced with AlN and SiC fibres.

Material	Content of elements, %				HRA	$\sigma_b$ , MPa	$K_{IC}$ , MPa m <sup>1/2</sup>
	Si	Al	N	O			
Sialon $C_1$	27,0	32,8	29,0	12,0	89	480	6,5
Sialon $C_2$	26,9	25,6	20,0	17,2	84	320	2,8
$C_1$ +30%AlN	-	-	-	-	87	600	8,0
$C_2$ +30%AlN	16,2	45,5	34,5	-	-	410	-
$C_2$ +30%SiC	-	-	-	-	91	420	5,6
$C_2$ +SiC (7- layered)	-	-	-	-	-	410	3,6

Although electron-microscopic studies testify that the structure of composites is not enough uniform, the fibres are chaotically desorientated, they do increase the bending strength and fracture toughness by 30-40%, preventing spreading of destructive crack.

In the layered material the destructive crack spread not along the phases border, but in fibrous layer still consisting considerable porosity after sintering.

# CERIUM-ACTIVATED SILICA GEL-GLASSES FOR USING IN SCINTILLATORS

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Ce-containing glasses are of interest as ionizing radiation detectors materials with increased radiation optical stability as well as light filters absorbing UV-radiation [1].

The cerium-activated silica glasses were prepared by modified sol-gel process. The source materials were tetraethylorthosilicate  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , hydrochloric acid (as a catalyst), aerosil (finely dispersed powder  $\text{SiO}_2$ ), cerium chloride and distilled water. The purities of the reagents were similar to those of analytically pure reagents. The process of synthesis incorporates tetraethylorthosilicate hydrolysis in water solution of the acid to obtain a sol, preparation of the colloid by adding aerosil into the sol, the addition into the sol-colloid system of cerium chloride, the neutralization of the activated sol-colloid system up to  $\text{pH} \approx 6.5$  by introducing an ammonia solution, liquid slip casting, gel-formation, drying and vitrification under equal temperature-time conditions of monolithic xerogels to a state of transparent glass, and inertial cooling. In parallel, samples were synthesized whose activation was carried out by impregnating the xerogels obtained with a water and a water-alcohol (2:8) solution of cerium chloride. The redox conditions of vitrification were varied by carrying out this process in air or in vacuum.

A spectral-luminescent study of Ce-containing silica gel-glasses doped at the sol stage and by impregnating porous xerogels with activator chloride salt solutions has been performed. The influence of the degree of doping and redox conditions of vitrification on the activator charge state and the content of hydroxyl ions and chlorine in the glass is considered. The preservation of the glass phase composition and the non-linear increase in the visible absorption intensity with increasing activator concentration from  $5 \times 10^{17}$  to  $3.0 \times 10^{20}$  ions/cm<sup>3</sup> are noted. It is concluded that there are two main types of optical centres. It is assumed that they represent Ce(III) oxygen complexes whose nearest surrounding includes quadruply-charged (the first type) and triply-charged (the second type) ions of cerium [2].

The scintillation efficiency of sol-gel silica glasses doped with cerium ions are discussed.

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### THE STRUCTURE AND PROPERTIES OF THE $\text{TiC}_x\text{N}_y$ -TiNi CERMETS BASED ON ULTRADISPERSE CARBONITRIDE TITANIUM.

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To improve physical-mechanical properties of the cermets on the titanium carbonitride base it is necessary to produce composite material with the smallest grain size of the refractory phase. To solve this problem different approaches can be used, in particular, the ultimate pulverising of the initial carbides[1]. However, under manufacturing of cermets by means of traditional liquid phases sintering technology the essential refractory grain growing occurs, so final carbide (carbonitride) grain size in the sintered alloys usually changes from one to several  $\mu\text{m}$ . In this connection the great importance have the development of compacting methods excluding the stage of liquid phase sintering.

This work presents the results of investigation of the structure and properties of alloys based on the  $\text{TiC}_x\text{N}_y$  - TiNi system produced from ultradisperse titanium carbonitride with using different techniques (sintering in the presence of liquid phase, hot-pressing under temperature below TiNi melting point, compacting under high pressure and high temperature and magnetic-impulse pressing).

The ultradisperse titanium carbonitride  $\text{TiC}_{0.5}\text{N}_{0.45}\text{O}_{0.05}$  with the average particle size 400 nm was the base of alloys. It was made by plasma recondensation of fabric carbonitride. The mixture of titanium carbonitride - titanium nikelide was grinded in planetary grinder in alcohol and compacted by one of the mentioned above methods. The samples of alloys were studied by X-ray, scanning electron microscopy and X-ray microanalysis methods. With using of automatic system of image processing the geometric parameters for microstructure (average grain size of refractory phase and length of TiNi-layer) were determined. With standard routine mechanical properties the hardness, microhardness and transverse rupture strength were measured. The results obtained allowed to reveal some correlations between manufacturing conditions, microstructure and properties of alloys under study.

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**SOL-GEL METHOD PREPARATION AND INVESTIGATION  
PROPERTIS OF SILICA POWDERS DOPED ORGANIC  
LUMINOPHORS.**

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In connection with increas of quantity of various products, being a subject to marks, the problem of protection them from forgery is very urgent. The most perspective decision of a given problem is the development of new types of mark means with using of organic and unorganic luminophors, as well as microdisperse materials with the various special additives, the availability of which is tested by physico-chemical methods. Thanking flexibility and opportunities of use of various initial substances, a sol-gel method is widely begin applied to obtain various disperse materials. This method is based on use of metal alkoxide connections, subjected to controllable hydrolysis in acid or alkaline environments [1,2].

As a result of researches some ways of reception doped silica powder with use various alkalis as catalysts hydrolysis ware developed on the basis of sol-gel method and them spectral-luminescent properties were investigated. Optimum luminophor concentration in the powder silica dioxide, which provides sure visual registration of luminescent at excitation with a UF-source of radiation with a main length of a wave 365 nm and capacity not more than 10 Wt is determined.

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**MATERIAL ON THE BASE OF COMPOSITE  $\text{Al}_2\text{O}_3$ -TiC.**

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The composite on the base of  $\text{Al}_2\text{O}_3$ -TiC find a broad using as cutting instruments, as well as are used as abrasive material. Difficulty of getting this material by the method of hot pressing enlarges a product cost and limits a form of cutting instruments.

The main purpose of work was a searching conditions of getting composite in the system  $\text{Al}_2\text{O}_3$ -TiC without operations of hot pressing. For the achievement putted purposes tended to get very active source components with using the following methods: 1) by the thermal decomposition organic derived aluminum and titanium; 2) by entering an additive of high disperse powder  $\text{Al}_2\text{O}_3$ , tinned on the base of cellulose and inorganic join aluminum.

As source components are used: commodity alumina marks "purity"; industrial titanium carbide; synthesized alkoxides aluminum and titanium (after the manner 1) [1]; nitrate aluminum (after the manner 2).

Use of alkoxides has allowed to get  $\text{Al}_2\text{O}_3$  active particles and  $\text{TiO}_2$ , which held up a growing of grain and promoted to the compaction a material. In work conducted comparative evaluation of influence organic derived aluminum and titanium (ethylate, amelate, heptylate, isopropylate and nonelate) carried in the amount 2-10 wt.% on the process sintering of composite  $\text{Al}_2\text{O}_3$ -TiC in conditions of inert atmosphere in range temperatures 1600-1800°C.

Installed that best homogeneity microstructure and density of sintering samples are reached without operations of hot pressing at the introduction to the quality of additives in the source composition of alkoxides titanium (ethylate titanium).

Additive of high disperse powder of alumina, tinned on the base of cellulose and nitrate aluminum promote a process of sintering and brings about increasing toughness in 2 times in contrast with checking samples (without the additive).

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# A CERAMIC COMPOSITE FROM BAUXITE

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A ceramic material with high mechanical properties that meet the requirement for engineering materials is obtained from white Timan bauxite (Komi Republic).

A chemical composition of bauxite is follows:  $\text{Al}_2\text{O}_3$  – 80-85%,  $\text{SiO}_2$  – 4-10%,  $\text{TiO}_2 \approx 6\%$ ,  $\text{Fe}_2\text{O}_3 \approx 4\%$ , other impurities is trace amount. So this composite may related to system  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{TiO}_2$ - $\text{Fe}_2\text{O}_3$ .

Boehmite is major phase formation mineral it have grain size  $< 1\mu\text{m}$ . Impurities of Ti, Fe, Si are present in crystal lattice isomorphously. During sintering (1350- 1380  $^\circ\text{C}$ ) the character of this elements distribution is conduct to the corundum phase. It provides densification and formation anisometric grains of  $\alpha$ - $\text{Al}_2\text{O}_3$ .

The solid- solutions of mullite and aluminium titanate are form during sintering between grains of  $\alpha$ - $\text{Al}_2\text{O}_3$ . The chemical formulas of the phases are follows;

$(\text{Al}_{1-x-y-z}\text{Fe}_x\text{Ti}_y\text{Si}_z)_2\text{O}_3, 3(\text{Al}_{1-x-y-z}\text{Fe}_x\text{Ti}_y\text{Si}_z)_2\text{O}_3 \cdot 2\text{SiO}_2$ , where  $x=0,0105-0,0174$ ,  $y=0,0075-0,0184$ ,  $z=0,0122-0,0274$ .

$(\text{Al}_a\text{Ti}_b\text{Fe}_c)_2(\text{Mg}_d\text{Ca}_k\text{Ti}_n)\text{O}_5$ , where  $a=0,46-0,72$ ,  $b=0,156-0,44$ ,  $c=0,02-0,14$ ,

$d=0,01-0,22$ ,  $k=0,015-0,02$ ,  $n=0,78-0,90$ .

Thus the obtained material has corundum matrix reinforced with mullite and aluminium titanate grains. A size of corundum grains are  $1+6\mu\text{m}$ . A glass phase are present as a film at the grains boundaries  $\alpha$ - $\text{Al}_2\text{O}_3$ .

A material has high reliable mechanical properties and obtained microstructures dissipate the crack energy effectively. Microstructure elements work as reinforcing, microstraining and microcracking, crack fixing and disorientating the crackpropagatione, crack- bridging toughening once. All of it built special dissipates complex in ceramic body.

Impurities and several special oxide and fluoride additives promote sintering and increase in the strength and resistance to crack of the alumina ceramics which is attributed to the special features of the microstructure.

**PRODUCTION OF TITANIUM SILICIDE CARBIDE  $\text{Ti}_3\text{SiC}_2$   
DURING SIMULTANEOUS CARBOTHERMAL REDUCTION OF  
SILICON AND TITANIUM OXIDES**

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The titanium silicide carbide  $\text{Ti}_3\text{SiC}_2$  belongs to relatively unknown group of complex carbides with laminar structure. The titanium carbide blocks consisting of  $[\text{Ti}_6\text{C}]$ -octahedra interleaves with hexagonal atom layers of the silicon in  $\text{Ti}_3\text{SiC}_2$ . Due to laminar crystal lattice  $\text{Ti}_3\text{SiC}_2$  shows plasticity and high fracture toughness ( $\sim 7 \text{ MPa/m}^{0.5}$ ) that are akin to the ones of metals and are not expectable for ceramics. The titanium silicide carbide is readily machinable, is not susceptible to thermal shock, has high strength characteristics ( $\sigma_{\text{bending}} \approx 600 \text{ MPa}$ ), and has good oxidation resistance comparable to chromium which is one of the most oxidation resistant metals. Such unique combination of properties allows to regard  $\text{Ti}_3\text{SiC}_2$  as a perspective material for design a new advanced structural ceramics with high operating characteristics.

At present there are two basic methods for preparation of  $\text{Ti}_3\text{SiC}_2$ . These are the elemental synthesis including self propagating high temperature synthesis (SHS); and chemical vapour deposition of titanium and silicon gallogenides (CVD). These methods are much expensive and are characterised by complicated production routine. It is also difficult to obtain the pure  $\text{Ti}_3\text{SiC}_2$ . As a rule the synthesis product contains some amount of titanium carbide and rarely silicon carbide or titanium silicides.

Our studies on simultaneous carbothermal reduction of titanium and silicon oxides under high vacuum conditions show that this process also could result in formation of  $\text{Ti}_3\text{SiC}_2$ . The  $\text{Ti}_3\text{SiC}_2$  synthesis occurs at temperature of  $1400 \div 1500^\circ\text{C}$  and gas pressure of  $10^{-1} \div 10^{-3} \text{ Pa}$ . At intermediate stage of reduction process the  $\text{SiO}_2$  converts to gaseous form of  $\text{SiO}$  and  $\text{TiO}_2$  carburazes to carbide  $\text{TiC}_x$  and/or oxycarbide  $\text{TiC}_x\text{O}_y$ . The gaseous  $\text{SiO}$  acts as transporter of silicon atoms to the titanium carbide surface, where the interaction between silicon monoxide vapours and chemically bounded carbon becomes more active. The interaction giving rise to silicon-enriched layers in titanium-bearing phases and finally formation of  $\text{Ti}_3\text{SiC}_2$  phase.

## GLASS-BASED OXIDE COMPOSITES – ANODES FOR LITHIUM-ION ACCUMULATORS

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Glass-based oxide composites are promising as the anode materials of lithium-ion accumulators, since they are distinguished by high capacity and reversibility at cycling over the potential range of 0-1.0 V.

Synthesis method enabling to produce the materials of  $\text{Sn}_2\text{BPO}_6$  composition was used.

The synthesized composites were investigated by X-ray diffraction method and the method of thermogravimetric analysis, IR-spectroscopy and electrochemically in a system with lithium electrode by the methods of potentiodynamic and galvanostatic cycling.

The effect of the nature of conducting carbon additive in electrode mass composition on specific and polarization characteristics of anodes has been determined.

The influence of the composition of nonaqueous electrolyte on the formation of surface layers and specific characteristics of synthesized materials has been studied.

The discharge characteristics of anodes based on graphite- $\text{Sn}_2\text{BPO}_6$  have two plateaus of discharge voltage within 100-200 mV and 400-500 mV ranges. The total discharge capacity ranges from 200 to 250 mAh depending on a cycle number.

The influence of SnO admixture in a glass composition on anode characteristics has been considered.



**Influence of  $\text{Ca}_2\text{CuO}_3$  and  $\text{Sr}_2\text{CuO}_3$  additions on the properties of bismuth-containing HTSC ceramics.**

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The distribution of defects of HTSC materials essentially affects their resistive and current characteristics. The dislocation lattice and oxygen vacancies may be considered as the defects which make the vortex lattice rigid at helium temperatures. However, with raising the defects working as effective pinning centers should be increased. Moreover, the necessity to create additional pinning centers in such materials may exist, and impurity phases seem to be possible sources for the formation of such centers.

In view of the abovesaid, in the present research the influence of  $\text{Ca}_2\text{CuO}_3$  and  $\text{Sr}_2\text{CuO}_3$  additions on the superconducting properties of  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  was investigated by measuring the electrical and magnetic properties of the ceramics, as well as by means of electron microscopy method.

$\text{Ca}_2\text{CuO}_3$  and  $\text{Sr}_2\text{CuO}_3$  in quantities from 0.3 to 10 mass.% were added to  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  powder with 80% content of the 2223 phase. Then the samples measuring  $3 \times 3 \times 10 \text{ mm}^3$  were tabletted and calcinated at  $t=850^\circ\text{C}$ .

These non-bismuth additions increase the density and reduce the porosity of the samples. The critical temperature changes nonmonotonically in the case  $\text{Ca}_2\text{CuO}_3$  additions. At the introduction of  $\text{Sr}_2\text{CuO}_3$  this value insignificantly decreases. The obtained composites are characterized by better transport characteristics: the value of  $I_c$  is twice as high, and the stability in magnetic fields up to 5Tl increased too, the latter fact being of a particular significance.

The data of electron microscopic investigation testify that in the presence of the non-bismuth phases the grain size decreases and the density becomes close to the one determined by X-ray method.

Thus, non-bismuth additions seem to favour the "strengthening" of bonds in the superconducting system and, consequently, contribute to the improvement of its superconducting properties.

**THE ANALYSIS OF CHEMICAL BONDING AND IONIC  
CONDUCTIVITY IN  $\text{Sr}_{4-x}\text{Nb}_{17}\text{O}_{26}$  ( $0 \leq x \leq 0.3$ ) BY THE EXTENDED  
HUCKEL'S BAND-STRUCTURE METHOD.**

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Recently synthesized compound  $\text{Sr}_{4-x}\text{Nb}_{17}\text{O}_{26}$  ( $0 \leq x \leq 0.3$ ) belongs to the group of metal oxides, called in the literature 'reduced oxoniobates'. It contains clusters of niobium monoxide and perovskite blocks with dimensions  $[2 \times 2 \times \infty]$ ,  $\{2 \times 2 \times \infty\}$  respectively. Earlier the investigation of the electronic structure of  $\text{Sr}_{4-x}\text{Nb}_{17}\text{O}_{26}$  ( $0 \leq x \leq 0.3$ ) has been carried out by means of the *ab initio* LMTO method. However, neither the electronic spectrum of  $\text{Sr}_{4-x}\text{Nb}_{17}\text{O}_{26}$  ( $0 \leq x \leq 0.3$ ) nor characteristics of chemical bonding were considered from the viewpoint of relations with the ionic transport properties. The existence of tunnels in crystal structure of  $\text{Sr}_{4-x}\text{Nb}_{17}\text{O}_{26}$  ( $0 \leq x \leq 0.3$ ) and the presence of homogeneity range permit to assume a possibility of the cation conductivity in this compound. We performed the analysis of the chemical bonding by using the extended Huckel's band-structure method. The calculations of the Mulliken's overlap population of the chemical bonds show a weak interaction between strontium and cubooctahedron of the oxygen atoms and the opportunity of strontium ion to move in the perovskite block along crystal axis *c*. The overlap population of the bonds Sr-O don't change near the Fermi level. It follows that the homogeneity range can be extended by doping with the alkaline ions. For instance, the Na cations could increase the ionic conductivity of  $\text{Sr}_{4-x}\text{Nb}_{17}\text{O}_{26}$  ( $0 \leq x \leq 0.3$ ). The oxygen's vacancies may appear in nonstoichiometric compound  $\text{Sr}_{4-x}\text{Nb}_{17}\text{O}_{26}$  ( $0 \leq x \leq 0.3$ ). The calculations show that the maximum probability of creation of oxygen vacancy is in the vertex of the oxygen octahedron of perovskite block. Moreover, the absence of the oxygen atoms in these crystal sites opens the additional way for moving of strontium ions the perovskite block. The strength of the Nb-O bonds (bond indices equal to 0.34-0.57) and to a less extend of the Nb-Nb bonds (0.212-0.29) provide a rigidity of the structure of  $\text{Sr}_{4-x}\text{Nb}_{17}\text{O}_{26}$  ( $0 \leq x \leq 0.3$ ).

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## 176 HG-CONTAINING HIGH-TEMPERATURE SUPERCONDUCTING CERAMICS

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Synthesis methodics for the Hg-containing samples of the  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+d}$  ( $n=1,2,3$ ) homological series has been proposed. It consists in using of  $\text{BaCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{CuO}$  and  $\text{HgO}$  as starting materials. It takes the possibility to prepare samples with the maximum contents of superconducting phase (>93%) [1].

Investigation of the quantity of superconducting phase dependence versus  $\text{BaCO}_3$  contains using data of X-ray, DTA and DTG-analysis has been done. Technological regimes for the precursors preparing have been optimized [2].

Different oxygen doping levels were provided by low-temperature treatments in reducing (Ar) and oxydizing ( $\text{O}_2$ ) atmospheres.

Conductivity and thermopower for such samples were measured for the electro-physical investigations of such materials.

Contactless inductive measuring on the alternating currents [3] took the possibility not only to receive an information about granulae critical state parameters  $H_{c1g}$ ,  $H_{c2g}$ ,  $J_{cg}$ , but also to found junctions type and to estimate intergranular environment critical state parameters  $H_{c1j}$ ,  $H_{c2j}$ ,  $J_{cj}$ .

Besides emphasized method, ceramic samples granularity was investigated by optical microscopy methods. Received values have been taking into account in the critical state parameters calculations for the Hg-containing HTSC.

Charge carriers distribution among structure elements of described objects has been investigated theoretically [4]. Key role of electrostatic interactions in superconducting properties formation has been founded. Energy spectra calculations for the Hg-containing HTSC have been carrying out with the aim of chemical bond nature investigation.

Results of the investigations of izo- and heterovalent replacements in cation subsystem influence on the critical state parameters and Hg-containing HTSC properties are shown.

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**SEMINAR F.**  
**COMPOSITES WITH THE METALLIC MATRIX**      **178-212**

## THEORY AND PRACTICE OF PROCESSES OF PRODUCTION OF BIMETALLIC CASTINGS ON THE BASIS OF IRON ALLOYS

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Application in constructions of machines and mechanisms of bimetallic castings (BC) allows to provide fullest combination of materials properties, differentiated by volume and surfaces of product.

As a result of research of physicochemical processes proceeding on the interphase boundaries of bimetallic pairs (BP) low-alloyed steel - high-alloyed cast iron (300C21M2 type) the basic oxidation-reduction reactions are disclosed, as a result of which solid-phase oxides such as FeO, Fe<sub>3</sub>O<sub>4</sub>, SiO<sub>2</sub>, MnO, Cr<sub>2</sub>O<sub>3</sub>, FeCr<sub>2</sub>O<sub>4</sub>, MoO<sub>3</sub> and gaseous products - CO<sub>2</sub>, SO<sub>2</sub> are formed. The effective refinement of interphase surfaces in the range of temperatures 900-1300°C is reached with the help of synthetic slags on the basis of systems Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-B<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>ZrF<sub>6</sub>-SiO<sub>2</sub>; Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-B<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>ZrF<sub>6</sub>-SiO<sub>2</sub>-NiO.

Results of researches allow to give an estimation to diffusive processes, to study structure and properties of transition layers of BP, to calculate effective diffusivities, including at exterior electromagnetic effect.

It is determined that at electromagnetic effect the increase of diffusive migration of atoms is observed, kinetics of mass transfer on boundary of partition solid - liquid (crystallising) metal is considerably changing.

Analysis of hydrodynamics of moulds filling at casting of BC testifies that they are determined by regularities of fluxion of molten metal in thin channels taking into account phase changes as a solution of the equations of heat balance.

Researches of temperature fields and conditions of solidification of BC testify to necessity of control of these processes with the purpose of stabilization of given parameters, lowering of tensions level.

Results of researches are assumed as a basis of development of industrial technologies and complexes of equipment for serial and mass production of BC, which application allows to reduce expenditure to 70 % of high alloyed steels and alloys, to increase in 2,0-4,5 times work resource of parts of machines and equipment.

## NEW TENDENCIES OF DEVELOPMENT OF ELECTRON - BEAM TECHNOLOGY

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Formation of Ukraine as independent economically developed country is impossible without generation of new technologies which will be competitive at the world market.

Method of high-speed electron-beam evaporation of metal and non-metal materials and further deposition them in vacuum - perspective base for creation of new technologies.

This method was successfully used in Electric Welding Institute named after E. O. Paton at the time of generation of industrial equipment and technology of deposition of protective coatings onto the gas turbine blades. But other possibilities of this method such as generation of industrial technologies to get massive billets from composite materials of dispersion-strengthened, micro-layered and micro-porous types were not demanded.

Industrial type of equipment and technology to get composite materials Cu - Y - Zr - Mo for electric contacts was generated in JSC "GEKONT", Vinnitsa, Ukraine. Structure, physical-mechanical and working characteristics of composite materials for electric contacts were investigated. Comparative working characteristics of used silver-based composites which were gotten with helps of methods of powder metallurgy and characteristics of condensated from vapor phase materials are enclosed. The most perspective spheres of using of condensated materials for electric contacts are pointed out.

The other important sphere which is developed in JSC "GEKONT" is electron-beam remelting of high-speed cutting steel scrap. Peculiarity of this developed in JSC "GEKONT" technology is strictly electron-beam remelting which is combined with heat treatment of metal. It gives a possibility to avoid hot cracking. Ingots from P6M5 which are gotten with helps of this technology don't need additional operations of forging and heat treatment and ready for production of milling cutters. Structure, mechanical and working characteristics of milling cutters which were gotten from ingots after electron-beam remelting are enclosed.

The other examples of using electron-beam technology for deposition of protective and wear-resistant coatings and special equipment for these goals are given.

### ECONOMICAL - REINFORCED CAST COMPOSITE MATERIALS

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Cast composite materials /CCM/ on the base of aluminium and cooper alloys have been developed and investigated, reinforced by non-metallic particles / for example, slag, petrurgical casting/, steel shots, elements of metallic debris. Debris of bronze and brass is employed for matrix formation . It was determined that firm-phase consolidation of thermodynamical non-consistent elements is possible under optimal thermal-time parameters and with applying exterior forces (vacuum, pressure). It were determined technological parameters of pieces production made of CCM.

Investigation and examination of new cast composites has shown, that CCM have hogher thermo-mechanical and tribotechnical charactéristiques, increased modulus, taht ensures increasung border temperature of stable work of CCM in the friction couple. CCM with matrix on the base of aluminium alloys, reinforced by non-metallic particles, on the above mentioned characteristics are on the level of composites, reinforced by high-expensive silicon carbides. CCM, in which matrix has formed as result of remelting of bronze debris, reinforced by steel shots, retain high stability and wear-resistance in the dry-friction regime, elevated loadings and temperatures up to 600 C.

Economical reinforced CCM and resources-savings casting technologies of cast pieces production are determined widening and efficiency of cast materials using in mass machine-building : from home goods up to metallurgy. Durability of tribological pieces made of CCM in 2-5 times more, than traditional mono-materials, that have been approved by production exploitation.

## INFLUENCE OF LASER TREATMENT ON STRUCTURE AND PROPERTIES OF MACROHETEROGEN COMPOSITES

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The present study examines influence of laser beam on the structure and tribological properties Macroheterogen Composite Materials (MCM). MCM composed by copper alloy matrix OCS5-5-5 - type that was reinforced by carbonic steel granules with diameter 0.8 - 1.0 mm. The MCM surfaces was treated by continuous CO<sub>2</sub>- laser with nominal level of power - 1 kW. During investigations it was changing power of laser beam (P) and density of power (Wp) by changing of diameter (d) of laser beam on treated surface and speed of moving of laser beam (V) also. Tests of friction and wearing was carried out by using the unit MT - 68 -type in conditions of dry friction and with lubricant. The pressure was changing from 0.6 to 1.8 MPa, and speed of sliding with continuously variable was near 4 - 12 m/sec.

The present study investigated the influence of density of power and speed moving of laser beam on the changing of depth of Zone of Laser Influence (ZLI). It's developed that after treatment took place the increasing (to 30%) microhardness of matrix alloy with connection between parameters of laser beam. Hypothetically it connected with diffusion mass transfer of iron, carbon and some other elements from reinforced phase to the matrix. In steel granules the hardened structures formatted with process of warming to the high temperature and short term cooling and hardness of these structures was increased to 4 - 5 times. The wear resistance of MCM increased to 1.5 - 2 times in comparison with initial composite material in connection with parameters of laser treatment.



## INVESTIGATION OF HYDRODYNAMICS AND HEAT-PHYSICS OF CAST COMPOSITE MATERIALS FORMATION

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Main hydrodynamics and heat-physics process which are occurring during obtaining of cast composite materials /CCM/ by liquid-phase combining have been investigated. By the mean of physical simulation and full-factor experiment it were investigated process of porous reinforcing sceletom infiltration, liquid matrix alloy flowing in porous channels, volume crystallization and cooling of CCM raw pieces in isothermic and non-isothermic conditions by liquid matrix alloys on the base of cooper and aluminium alloys.

It were cleared main technological parameters , influencing on infiltration kinetics : geometrical and linear characteristics, mutual orientation and wettebility of reinforcing elements by liquid matrix alloys, density, visconsity and surfece tension of matrix alloy. It were described main technological process /wettability, surface flowing of matrix alloy, flow-through of liquid phase/ which occured in channels of porous sceletom. Simultaneously it were investigated flowing regimes of matrix alloys under obtaining of CCM of various contents under gravitational infiltration and under pressure with applying vaccum.

As a result of carried-out investigations it was optimezed structure of cast composite materials, reinforced by high-modulus and discrete particles on the base of cooper and aluminium matrix alloys and technologies of cast pieces obtaining with regarding of influencing of hydrodynamical and heat-physical process, occuring during formation of CCM.

PLATED BORON ALUMINIUM COMPOSITES  
USED IN AIRCRAFT STRUCTURAL ELEMENTS

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Development of materials with optimized structures in terms of improving their processing properties for constructional element application is a mostly effective way of employing high properties of boron aluminium composite materials (CM), as shown in this work. This way provides retention of mechanical or service characteristics at rather high level. These are reached by the use of plated layer of high strength alloys having an appropriate distribution of boron fibers through the matrix bulk, introduction of nets, etc. Various versions of plated layer with elevated strength were considered. An advantage was shown when toughened aluminium alloys were used as plating materials.

Relationships were established of the boron aluminium CM strength and relative thickness of the plated film of AD33, D16 and D20 alloys. Experimental relationships were found between the properties of a plated CM and processing parameters during the operations of bending of a sheet material, the contact spot welding, the diffusion welding of CMs with titanium alloys, and riveting processes. Methods of mathematical statistics were used to construct analytical models describing relations of minimum bending radius (tensile and fracture strength of the welding point) and parameters relative to the laying of the reinforcing fibers and thicknesses of plated layers of a bended (welded) preform of CM.

The works carried out were used to determine a field of an effective application for boron aluminium CMs in components and elements of constructions subjected to static, dynamic or cycling loadings. Such components made of boron aluminium CMs as profiles, pipes, or constructional elements like panels, braces, knee braces, etc, can increase their service life 1.5 to 2.0 times with the reduction of the weight up to 20 to 60%.

NEW COMPOSITE ALLOYS ON COPPER BASE AND  
TECHNOLOGICAL PARAMETERS FOR PRODUCING OF CASTING  
BLANKS

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Over the last decades increased interest the contributors of many countries exhibit to alloys which are characterized by miscibility gap in a liquid state. It is connected to essential possibilities of management of structure forming in such alloys because the melt for want of certain temperature parameters is emulsion with inclusions of a disperse phase. Last ensure essential influence on structures forming.

The certain inclusions can play a role of lubrication ensuring "wearless" process. The sizes of inclusions of this phase can be rather large propotional to sizes of strengthening phase (up to 1000 nm). Other inclusions ensure process of strengthening of a main material. In this case requests to a dispersibility character of distribution and structure of such inclusions are much higher.

The multicomponent alloys of copper - (Fe - Cr - C) - alloy system concern to number of advansed compositions. The copper alloys with a structure of a type " frozen emulsion " in which strengthening a phase is a chromium pig-iron are characterized by high thermal stability in the extreme operating conditions. The mechanism of inclusions forming is emulgation of a melt in miscibility gap for want of temperatures close to temperature of binodal for want of superposition of external effects.

The main complexity of producing of items from such alloys is a maintenance in their structure of necessary dispersiblis inclusions uniformly distributed on all volume. Due to a selective operation of electromagnetic fields on liquid phases with various electroconductivity forms and the relative velocity of phases is adjusted the ratio of their "apparent" specific gravity is changed. Excitation of pulsing force effects with the certain frequency on interphases surface allow actively to influence on process of a dispersion of a liquid metal medium.

### NEW COMPOSITE MATERIALS ON THE BASIS OF ALUMINIUM

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A series of composite materials on the basis of aluminium obtained by the method of mechanical alloying has been developed [1]. The materials contain up to 20% of the alloying component, retaining herewith the ability to hot compacting and plastic deformation.

Among the alloying components tested are silicium carbide, aluminium oxide, REE and their oxides, boron, scandium and some others.

From all the tested materials, compact samples were obtained with the density not less than 96% from the additively calculated density of the respective substances, which were then subjected to plastic deformation. The degree of deformation on different samples was 60% to 360% without breaking of the sample. For some of the materials the mechanical properties were measured. The example is given in the Table.

Mechanical properties of samples of a material  
containing 20% boron.

Ultimate strength MPa	Yield strength MPa	Mod. of elonga- tion %	Reduc- -tion of area %	Modulus of elas- ticity MPa	Hard- -ness MPa	Limit of endura- nce MPa	Coef. of therm. expans. 1/°C
210	150	4	6,6	79	80	90	16,0×10 <sup>6</sup>

Moreover, some of the materials obtained were tested for weldability with argon-arc welding. The tests proved good weldability and the absence of cracks in the near-the seam zone.

The results obtained allow to anticipate the creating of structural and other easily producible materials with unique properties.

1. Freidin B.M. et al. Method of producing an alloyed powder on the basis of aluminium. RF Patent N2113941. Priority of 29 July 1997.

## ALUMINIUM BASED ANTIFRICTION MATERIALS

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Elaboration of the new antifriction materials for aircraft construction and for working in cosmos assumes ever-greater importance in last years. Materials, which are used in these fields of engineering, must possess small specific weight. Aluminium and aluminium alloys are corresponding to this requirement.

The powder metallurgy method opens wide possibilities for creation of modern composition materials. However aluminium processing by powder metallurgy method is limited by firm aluminium oxide film on aluminium powder parts.

This work is devoted to obtaining of composition antifriction materials in which porous frame and metal base are made from aluminium.

Porous aluminium frame forming is realized by method of hot pressing in jacket which is more technological and reliable in comparison with method of hot pressing in mould.

To determine the optimum regime of porous aluminium frame forming the influence of temperature and pressure on quality of sintering was investigated.

Quality of briquette was determined according to data of impact strength, hardness and shear strength measuring.

Working out the technological method of obtaining of porous aluminium allows to receive one-layer and two-layer products in which low-porous based layer must be manufactured with porosity up to 5% and high-porous layer – with porosity 30 – 70%. Thickness of high-porous layer must be minimal but not less than allowed limit of linear wear of product.

## CAST COMPOSITE MATERIALS ON THE BASE OF ALUMINIUM WITH DISPERSED PARTICLES

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The aluminium alloys reinforced with dispersed particles of graphite, carbide of silicon, oxides of silicon and aluminium have a lot of unique properties despite of lowered physical-mechanical characteristics. Altering the kind of introduced particles, their size and quantity, we can heighten of the essence tribotechnical and damping properties, hardness, high-temperature strength and decrease the coefficient of thermal expansion.

The influence of alloyed elements and regimes of obtaining and heat-treatment to the structure, tribotechnical, damping characteristics and corrosive resistance of obtained materials has been investigated. In the alloys of systems Al-C and Al-SiC the carbides of aluminium arise at the temperature higher of 500°C in the structure of the alloys and vastly decrease corrosive properties.

The considerable alteration of properties and character of interphase interaction in the system Al-C depending of concentration of silicon has been found. In the region to 20 mass % of silicon the formation of carbide of aluminium arises predominately and in the region of alloys with content of silicon more than 20 mass % the carbide of silicon forms itself for choice.

The liquid phase methods of introduction of dispersed particles to the melt and the technology of obtaining of composite materials and castings have been developed. The uttermost values of the temperature, pressure and chemical composition of the alloys, providing the regulated introduction of the particles to the melt, have been determined. The technology permits to obtain materials containing to 60 vol. % of dispersed particles with the size from some microns to some millimeters.

Developed materials can be used for manufacturing of jobs subjected wear, sliding electric contacts, wares with low coefficient of thermal expansion.

### **Research diffusion of interaction in the fibre-reinforced CM of system an alloy Chromium -SiC**

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The creation of the fibre-reinforced composite materials (FCM) of system plastic a heat resisting alloy chromium - carbide of silicon has required detailed study of processes of high-temperature physic-chemical interaction of fibres SiC with a metal matrix.

The researches have shown, that the satisfactory stability of system Cr-SiC is observed only at temperatures up to 1000-1050°C. The reduction of a degree of interaction of fibres with a matrix is achieved at the expense of application antydiffusion of barriers. A choice of structures of effective barriers made with the help of a complex thermodynamic calculation and experimental research systems. By thermodynamic researches is established, that in systems Cr-Zr (Hf) C and Cr-Zr (Hf) N in an interval of temperatures 1200-1500°C the interaction should not occur. The experimental researches have confirmed absence of appreciable interaction in these systems.

In systems SiC-Zr (Hf) C the formation is revealed at 1300°C for 50 h. challenger layer of complex structure. It is caused nonstochiometric of samples SiC (surplus Si), and also lack C in carbide ZrC, HfC. The of drawing a thin layer of carbon. Thus, the maintenance of a necessary level of physic-chemical stability FCM Cr-SiC is possible only under condition of drawing on fibres of dividing layers from ZrC and HfC. elimination of interaction in systems Zr (Hf) C-SiC is reached at the expense

**OPTIMIZATION of STRUCTURE FORMATION CONDITIONS of  
BIMETAL "STEEL - BRONZE" with POWDER WORKING LAYER  
during HOT FORGING**

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Bimetals of the type "steel - bronze" is widely used as antifriction materials. One of the most effective methods of bronze layer deposition on the steel base is welding by explosion. In spite of technological simplicity of this process realization it is not always possible to realize its adoption in the conditions of machine-building plant.

One of the most perspective ways of bimetal (BM) production is hot pressfit powder working layer on compact (or powder) steel base. It is necessary to create temperature gradient in preform body in order to provide high splicing quality of BM heterogeneous materials during hot forging (HF). In this case the possibility of optimal deformation condition providing for each layer is presented.

On heating preforms to temperatures below melting temperature of bronze BrOTsS-5-5-5 the splicing quality of BM layers is low. Optimum results were obtained during heating which provided melting of bronze layer with 0.5 - 0.8mm thickness near separation boundary. On condition that melting zone depth increases, the foliation takes place near the upper preform end fitting to the upper punch. It is stipulated by the reverse segregation of tin and cooling of pointed zone during HF. So, preform heating with the temperature gradient allows:

- to provide qualitative splicing of BM layers;
- to prevent reverse segregation of tin and material foliation in preform zone, fitting to the upper punch;
- to save inclusions of structure free lead in the upper preform zone and antifriction properties of bronze.

But even on condition of melting zone localization we cannot exclude the possibility of tin penetration to the separation boundary. This fact reduces strength of layer connection. It is suggested before cold pressfit to spray copper layer of 0.2 - 0.4mm thickness onto steel base in order to prevent such effect. On condition of following heating tin, penetrating from upper layers, is dissolved in copper and in structure free condition is not discovered.



## WEAR RESISTANT ALUMINIUM MATRIX COMPOSITE MATERIALS

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The ever improving area of engine building for aircraft application requires development of advanced composite materials (CM) to be used in radial or end seals. As revealed the analysis of available metallic antifrictional materials used under elevated temperatures and/or loads, for these conditions, compositions are useful based on high-temperature casting aluminium alloys filled with refractory particles.

Casting AL-7-alloy based wear resistant CMs were developed. To reduce the friction loss, boron nitride was used, while wear resistance was increased by the introduction of alumina into a material. Samples of CMs were prepared by liquid phase impregnation on the vacuum-compression impregnation unit.

These materials when tested on wear resistance behaviour, showed high values of tribological characteristics. For composition of aluminium - alumina particles, the coefficient of friction was 0.2, wear rate was not above than 3 mm/km that corresponds to the level for the materials based on graphites of "Nigran" and AG-1500 types.

The materials are good to be used for end seals under conditions of boundary-layer friction and high contact loadings.

### FUNCTIONAL NITROGEN-ALLOYED POWDER ALLOYS

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Compositions and a technology of producing iron-base functional alloys by the method of powder metallurgy have been developed by the Institute. The role of the strengthening phase is played by high-strength, heat-resistant nitrides of vanadium, silicon and chromium. The basis for this technology is the process of isobaric saturation of powders of iron-nickel alloys, alloyed additionally with strong nitride-forming elements, in the atmosphere of compressed molecular nitrogen, followed by hot extrusion. This method allows the saturation of powder alloys with nitrogen up to 3% by mass exceeding its equilibrium concentration by several exponents. As electron microscopical analyses have shown, the structure of alloys represents a composition which consists of the austenite matrix providing operating properties of powder materials (such as minimum temperature coefficient of linear expansion  $TK_{LP}$  and temperature coefficient of frequency  $TK_f$ ) with uniformly distributed dispersed nitrides. Functional powder alloys with the following properties have been produced on the pilot plant at the TsNIIChermet's experimental base:

- the powder alloy H33X4C2K2A1 of Invar-type with nitrogen content of 1.23% by mass in the form of complex nitrides on chromium and silicon base has the  $TK_{LP}$  of  $4.8 \times 10^{-6} \text{ grad}^{-1}$  within the temperature range from 20 to 200°C and the hardness of 40÷44 HRC;

- the powder alloy H24X9Φ4A3 of Elinvar-type with nitrogen content of 2.99% by mass in the form of the complex nitride VCrN (15-20% by volume) is characterized by 3.5-fold higher strength than of classic cast Elinvar alloy ( $\sigma_{0.2} = 630 \text{ MPa}$ , 40÷42 HRC) at the comparable  $TK_f$  of  $(40 \div 80) \times 10^{-6} \text{ grad}^{-1}$ .

The present work is covered by RF patent.

# NEW HIGH-STRENGTH DUCTILE A POLYMATRIX COMPOSITE MATERIAL ON THE BASIS OF BCC REFRACTORY METALS

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The results of a research of mechanical properties, for the first time created by us, of refractory polymatrix composite materials with high strength and satisfactory fracture toughness are represented.

The combination of high strength and satisfactory fracture toughness of an composite material is achieved by means of armoring of a layered matrix of a system Cr-V by high-strength fibers from alloys of tungsten.

Is shown, that the high-strength properties of a layered system depend on a bilayer thickness  $\lambda$ . The sharp magnification of a yield point in this case is observed for the thickness of  $\lambda < 8,5 \mu\text{m}$ . The marked magnification of strength is much higher at the high temperatures, than at the room temperature. So, yield point ( $\sigma_{0,2}$ ) of the layered system with a diminution of a thickness bilayer  $\lambda$  from 80 to 1,2 microns increases at the room temperature up to 804 MPa. It is more than the yield point significance of a base alloy almost three times. At the temperature of 1373 K yield point reaches 262 MPa. It is more than the yield point significance of a base alloy almost five times. It is important that in an interval of a modification of a bilayers thickness, where the strength is sharply increasing, plasticity is satisfactory. The specific elongation ( $\delta$ ) reaches 15%. Stress concentration factor ( $K_Q$ ) does not decrease and even has the tendency to growth ( $K_Q = 25-37 \text{ MPa} \cdot \sqrt{m}$ ). It is important also that with a diminution of a bilayer thickness  $\lambda$ , rate of a steady-state creep sharply decreases and stress-rupture strength at the cyclic loading considerably increases.

The further increase of strength and fracture toughness of a layered composite material is achieved by means of armoring by high-strength fibers. In the result of armoring of the layered polymatrix the high-strength and ductile composite sheets is obtained. Sheets can be deformed by means of punching, rolling and flexing.

So, when the volumetric share of fibers is 20 %, a yield point at the temperature of 1373 K reaches 620 MPa, and ductile-brittle transition temperature is 273-283 K. Stress-rupture strength (hundred hours) at the temperature of 1273 K exceeds 120 MPa ( $\sigma_{100}^{1273} > 120 \text{ MPa}$ ).

The obtained materials can be used for nuclear reactors, in the engines production and rockets production.

## STRUCTURE AND HOT HARDNESS OF POWDER COMPOSITE MATERIALS WITH COPPER MATRIX

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The electrodes serviceability, which are a removable tool of contact welding machines, is the main factor determining productivity of welding and quality of welding joints. Usually the electrodes are produced from casted electroconducting materials with copper matrix of dispersion-strengthened or precipitation-hardening types. The powder composite materials received by porous W infiltration with Cu or alloys on the copper basis (with Ag, Ni, Co, Ce, Ti, Al) was chosen as object of the investigation. Electrodes stability is known to correlate to mechanical properties including short-term and long-term hardness of materials and to loss of strength characteristics (the loss of strength beginning temperature, the temperature of 50% properties decrease). Therefore in the work the structure, phase composition, hardness and temperature dependence of the composites short-term hardness have been investigated.

With the complex structure analysis a matrix character of the composites contained 50-70% wt. W is established. The choice of alloying additions is shown to provide the matrix formation as precipitation-hardening or dispersion-strengthened component. It is ascertained that by way of the influence increase on the hardness the alloying elements can be arranged in the following order: Ni, Co, Ag, Ce, Ti. In the same direction the temperature, at which mechanical properties decrease on 50% value, is increased. It is found out that such properties change is stipulated by influence of the matrix intermetallic reinforcement. The loss of strength rate of the W-Cu-Ag composite considerably is decreased under the intermetallic TiAl influence. As a result of this effect and at the temperature 700°C decrease of the hot hardness reaches only 33,4% value. The directed structure efficiency of the structure and the properties is confirmed by the positive results of the serviceability investigation of the contact welding machines electrodes.

PHYSICAL AND MECHANICAL CHARACTERISTICS  
ANTIFRICTIONAL COMPOSITE MATERIAL ON A BASIS BRONZE,  
REINFORCED BY DETONATION DIAMONDS,

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The creation composite of antifrictional materials with increased for the resource of the pair of friction is a urgent task. By the authors together with firm "Composite", Ltd of Kyiv is developed a antifrictional composite material on a basis Cu-intermetallics with tin and zinc reinforced by diamonds of detonation synthesis with the size 5-50  $\mu\text{m}$ . As against existing of antifrictional materials, where alloys is not connected to matrix structure the new composite contains ultrasmalldispersive of a particle of diamond in structure intermetallics. Due to presence of diamond the antifrictional material has high heat conduction, that interferes with occurrence of high local temperatures in a zone of friction and provides increase the resource of pair of friction.

The influences, executed earlier researches, of concentration diamond alloys in a composite material on it of the tribotechnical characteristic have shown, that the increase of concentration of diamond essentially influences the physical and mechanical characteristics of a composite improving thus of the tribotechnical property of a material (Table 1). The experiment is confirmed, that the increase of the contents alloys by a diamond component reduces factor of friction in some times, and carried out of laboratorial test of a material simulating work of a support drill bit, confirm increase the resource of pair of friction in 1,5-1,7 times.

Table 1

№	Performances	The contents of diamond alloys	
		5 vol. %	10 vol. %
1	Density, $\text{g/cm}^3$	5,10	4,86
2	Hardness, HRB	45-50	65-70
3	Strength for want of rupture, MPa	120-130	50-70
4	Strength under bending, MPa	170-190	140-160
5	Strength for want of compression, MPa	340	390
6	Relative elongation, %	5-5,5	2-2,5
7	The module of an elasticity under bending, MPa	36400	42500
8	The module of an elasticity dynamic, MPa	25800	21000

Thus increase of the contents diamond alloys renders the certain influence to physick-mechanical performances of an aggregate, improving for want of it tribotechnical properties of a material.

### Modern bio-compatible alloys on the cobalt-chromium basis

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Two bio-compatible alloys on the cobalt-chromium basis, new in their nature, have been elaborated recently in Ukraine. They are called «Ceradent» & «Plastocryst». These alloys successfully passed a range of tests according to the demands of International Standardization Organization. There were such tests as: medical, biological, toxicological, technical & clinical. Both materials, that by the way are included in the register of medical products approved by the Ministry of Health of Ukraine in accordance with the level of technical characteristics can be used for casting & dismantled dentures production.

Tests conducted in the Institute of Material Acknowledgment Problems of NASU proved, that the «Ceradent's» endurance is similar to oxide aluminium ceramics ( $Al_2O_3$ ) and it exceeds the endurance of titanium alloys VT5-1, VT6, VT14, VT16. Owing to these properties, new alloy can substitute endoprostheses that are made from these materials.

Comparative tests on endurance during friction of such couples as polyethylene «Hyrulen»-titanium, polyethylene-ceramics  $Al_2O_3$  & polyethylene-«Ceradent» has been conducted under conditions close to the natural.

Initial roughness (asperity) of the titanium & Co-Cr-alloy was estimated at  $Ra=0,05mm$ . Constant load created by contact efforts of  $5N/mm^2$ . Slip velocity was  $0,1m/s$ , test lasted 20 hours, environment of materials disposal was a physical solution,  $t=37^{\circ}C$ .

Wear out was controlled by the quantity taken during a polyethylene friction. Weight & linear variations of ceramics  $Al_2O_3$ , polyethylene «Hyrulen», titanium & Co-Cr alloys were also measured.

The biggest wear out of polyethylene «Hyrulen» was fixed in couple with Titanium VT5-1, while wear out was followed by the friction path's appearance on the titanium circle & considerable enhancement of the surfaces roughness (asperity). In conclusion of every test cycle wear out of the titanium circle measured within 5-8 mm. Wear out of the ceramics & Co-Cr casting circles was not fixed.

**Littleactivated temperature-corrosionresistance radiatingstrength a composite material on a basis of Chromium.**

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The results of complex researches on creation of a new class viscous radiostrength littleactivated of composite materials on a basis of Cr for environments TVEL and TVS nuclear power reactors on fast neutrons are submitted. The results of study of influence addition V to alloys Cr and Cr to alloys V on structure and properties in a wide interval of temperatures are described. The structures of alloys making GCM are determined in which the optimum combination high temperature corrosion of stability, high temperature strength, low temperaturat and technological plasticity, and also radiating resistance is reached.

Theoretically and experimentally is investigated diffusion interaction, and also feature of deformation and destruction of samples GCM in a wide interval of temperatures in initial and irradiated condition.

## BORONIZING of HOT-FORGED POWDER STEELS

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To the present day the application of chemico-thermal treatment in the manufacture of powder parts was limited by carburizing, carbonitriding and steamoxidizing. Sometimes chroming, boronizing, siliconizing were used. But applying to hot-deformed powder materials boronizing was not practically studied.

In the paper regularities of solid and liquid phase saturation with boron of porous and high dense hot-forged powder preforms on iron base are investigated. Differences of this process from compact material boronizing are defined. Higher structure defectiveness of powder materials stipulates larger depth of boronized layer in comparison with cast steels. At the formation of liquid phase boron-content eutectic it is infiltrated in limited depth of porous preforms. In this case eutectic emergence on the item surface takes place significantly later than at boronizing of hot-forged powder and compact cast preforms.

In the boronizing process on the preform surface continuous layer of borides  $FeB$  and  $Fe_2B$  is formed. Under this layer sublayer and transitional zone are situated. In solid phase saturation sublayer represents boron ferrite with boride inclusions, and during saturation in the presence of liquid phase represents eutectic ( $\alpha-Fe+Fe_2B$ ). Transitional zone is formed at steel saturation on the account of driving away carbon by boron into item core. The depth of this zone is defined by the carbon content in the material, and its composition is on eutectoid level. It is established that in order to obtain defectless items with required precision and satisfactory surface finish of face and side planes it is necessary to carry hot repressing of boronized preforms in the presence of liquid eutectic phase in surface layer. Materials and items, where wear resistance exceeds surfacing material U30H25RSG resistance at dry friction and abrasive wear are obtained. Corrosion resistance of these materials in the solutions of acids and alkalis is on a par with the steel 12H18N10T.



THERMODYNAMICS OF FORMATION OF SCANDIUM – IRON  
COMPOUNDS

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The Sc-Fe phase diagram was first studied in [1]. According to these results, the Sc-Fe system is characterised by two compounds:  $\text{ScFe}_2$  (melts congruently at  $\sim 1873$  K) and  $\text{Sc}_3\text{Fe}$  (forms peritectoidally at 1073 K). The crystal structure of  $\text{Sc}_3\text{Fe}$  was not established in [1]. The data available in the literature for the  $\text{ScFe}_2$  compound are conflicting. Later, the Sc-Fe system was re-examined, and a refined version of the phase diagram in the concentration interval 0-90 at. % Sc was proposed [2]. The  $\text{Sc}_3\text{Fe}$  phase [1] was not observed, while the compound with the approximate composition  $\text{Sc}_7\text{Fe}$  was found. Later [3, 4], composition of this compound was shown to be  $\text{Sc}_{29}\text{Fe}_6$ .

In the present work, thermodynamic properties (Gibbs free energy, enthalpy and entropy of formation) of  $\text{ScFe}_2$  (930 – 1030 K) and  $\text{Sc}_{29}\text{Fe}_6$  (720 – 960 K) were studied by means of e.m.f. method. For  $\text{Sc}_{29}\text{Fe}_6$  low thermodynamic stability is observed compared to the neighbouring phases  $\text{ScFe}_2$  and  $\langle \text{Sc} \rangle$ . The results obtained are discussed, together with the literature data as well as with Miedema estimations.

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# ORGANIZED METALLIC FIBROUS STRUCTURE-BASED VIBRATION DAMPING ELEMENT BEHAVIOUR

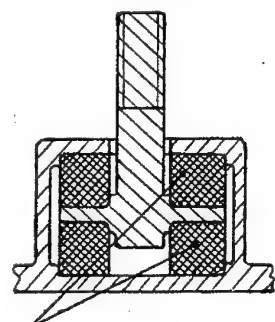
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The available traditional damping materials and products have disadvantages and when undergone to unordinary loadings or under extreme conditions, they can not provide vibration protection.

Researches made by the Institute for Problems of Materials Science, NAS of Ukraine, have shown that the above requirements can be met if the damping materials and products are made using a technology based on continuous metal fibers subjected to a joint consolidation into organized anisotropic structures with macromoving elastic elements. They are able to efficiently withstand high drops of power loadings being stable under aggressive media, non-inflammable and lightweight.

Experimental damping elastic elements based on metallic fibers were made in the form of inserts, intended for the use in vibration damping fittings of power stations, in particular, for jet-propulsion engines. The Figure shows damping elements located into an engine fitting.



Damping elements

The test results of fittings to measure damping characteristics and durability under loads similar to actual operation of an engine revealed that metallic fiber damping elements ensure a damping level that is not lower as compared with traditional rubber ones, but within a broader range of temperatures, they feature an increasing limitation of the pathway, high carrying ability while their spring-actuated move only slightly increases.

Further investigations of relations between structural parameters and characteristics of the metallic damping elements will provide methods of monitoring properties and their optimization for products designed for specific functional applications.

## STRUCTURES AND SOME PROPERTIES OF WHISKERIZED SILICON CARBIDE FIBERS

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Silicon carbide fibers were produced by chemical-thermal treatment of felt-like hydrated cellulose, woven or knitted structures. The treatment was accompanied with a growth of SiC whiskers upon the fiber surfaces due to the silicon-comprising medium formed. Compositions and structures of whiskerized silicon carbide fibers were examined using chemical and spectrum techniques, electron microscopy, X-ray radiography and electronographic analyses.

X-ray and electronographic analyses showed that SiC fibers made of hydrated cellulose precursor feature a polycrystalline structure of  $\alpha$ -modifications with the grain size of 0.10 to 0.15 micrometer. SiC fibers have 2 to 3 mm diameter, density is 2.6 to 2.7 g/cm<sup>3</sup>. SiC whiskers had 0.10 to 0.15 micrometer in cross-section, their lengths can be varied by the synthesis conditions (using catalysts, varying composition and gas flow rate) and can reach several centimeters. The whiskers have the structure of  $\alpha$ -SiC. The peculiarity of whiskers is a narrow range of their cross-sections as defined by the structural properties of a substrate. Arrangement of the whiskers on a substrate and their growing direction can be adjusted by the use of various woven structures in order to produce polycrystalline fibers.

Whiskerized SiC fibers were used as reinforcement of aluminium alloy Al-12%Si to estimate their physico-mechanical properties. Composites were prepared by the vacuum impregnation of a SiC felt that comprised around 50 % of whiskers, using the above alloy. Results of mechanical tests have shown high physical and mechanical properties of the fibers developed and opportunities to use them as reinforcing fillers for a variety of composite material application.

**THE SIGNES OF PRESENCE OF A SELF-ORGANIZED LATENT-CRYSTALLINE PHASES AFTER THE TYPE OF CTC /KPZ-rus./ AND A ROLE IN FORMATION OF AN ANOMALY PROPERTIES FOR THE 3d-METALLIC ALLOYS**

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For the first time the physical-chemical nature of the self-organized latent-crystalline phases after the type of the Charge Transfer Complexes (/CTC/, are initiating an anomaly properties of the 3d-metallic alloys), were identified and investigated by the author [1-4, IMSP of Ukr.NAS]. It was determined [1], that CTC-clusters are defects of chemical nature in the 3d-metallic alloys, accumulated on (110), (112), (111)\* crystallographical planes of the alloys grating. CTC-clusters from 3d-alloys have the similar properties and special features as one from chemical combination (a d-metal complexes with transfer of charge that are synthesised in free state). They have a nonsaturated nonvalency chemical bonds and autocatalitical activity of CTC-cluster; a short interatomic bonds Met-Met into central ionic of CTC-cluster; crystallogometrical peculiarities and autocatalitycal activity [3]. The nonsaturated nonvalency chemical bonds of CTC-cluster formate a dislocatin nets, tangles, subboundary in crystals; CTC are forcing the local corrosion centres; one are placing a second-crystallical forms in alloys. With the Coherence of an alloy latice and the big CTC-clusters has done by directed stretch bonds after the Met.-Coval. type, the CTC-contained alloys have highest embrittlement and intergranular strengthening [4]. The metallographical, chemical, physical signes of the CTC-manifestations (in alloys on the basis Cr, V, Ti, Fe etc. metals) after a test investigations will have discuss. The science manipulation by properties of the self-organized latent-crystalline phases after the type of CTC will be helping for decision many scientific problems of Solid State Physic. of Synergetic and for Technological of a new materials.

\*The 3d-electrons of  $t_{2g}$ -orbitals place in the (111) and form a short-range order in a cubic grating.

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SYNTHESIS OF METASTABLE COMPOUNDS IN NON-EQUILIBRIUM DYNAMIC SYSTEMS AND THEIR FUNCTIONAL PROPERTIES

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Complex physico-chemical systems in non-equilibrium conditions can act as a source of forming new dynamic states, namely dissipative structures which are adequate for a certain form of supermolecular organization. Such type of stability is due to non-linear interaction of several chemical processes with feedback, available diffusion and all other attendant thermo-kinetic effects. All this causes a broad gamot of autolocalized states inside a reaction zone, a solid heterogenous or powder chemical system. On the basis of present knowledge it is most likely to occur the formation and stable existence of metastable phases in such systems.

As the dynamic systems there were chosen non-equilibrium powder compositions 'transition metal- chalcogen' containing elements (carbon, silicon and boron) which are the most active reducers of oxides and chalcogenides in equilibrium conditions.

It was determined by methods of microroentgen analysis the formation of multicomponent phases  $Me^I - Me^{II} - Si(C) - Se$  and  $Me^I - Me^{II} - Si(C) - S$  under composition's sintering in a temperature interval of active chalcogenide reduction by silicon and carbon under equilibrium conditions.

The developed compositions on base of high-temperature steels containing metastable phases in small proportion have considerably higher wear resistance compared to equilibrium analogs.

THE STRUCTURE AND TRIBOTECHNICAL PROPERTIES OF THE  
CERAMIC - METAL MATERIALS BASED ON HIGH-MELTING  
TITANIUM COMPOUNDS.

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The new antifriction ceramic - metal materials of frame -type using as hard component of titanium boride and nitride and bonding agent for copper-nickel alloys have been developed.

The materials are produced by clinkering of the porous frame from high-melting compounds including graphitization lubrication with the subsequent its impregnation by the bonding alloys.

The kinetics of the process for the impregnation of the porous frames by the copper-nickel alloys has been investigated and the conditions of the qualitative impregnation have been determined.

The structure and physico-mechanical properties of the materials obtained have been studied.

The tribotechnical properties of the developed materials during the friction together with the chilled steel within the load interval 1 - 20 MPa and the speeds up to 30 m/s under the conditions of limiting and dry friction have been investigated.

The mechanism of the composite wear and destruction at dry and limiting friction in the mentioned range of loads and the slip speeds has been established.

The perspective for the use of the ceramic - metal materials in the friction units of the production internal combustion engines has been evaluated.

INVESTIGATION of PECULIARITIES MELTING REFINING and  
CRYSTALLIZATION of CAST REMAKE STORAGE from HIGH  
PURITY ZIRCONIUM ALLOYS

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The scientific researches of peculiarities of obtaining of high purity radiation - resistant zirconium alloys of high homogeneity of a chemical composition, with the minimum contents of impurity inculcation (summary contents  $< 0,1\%$ ), and also method of obtaining from them storages with uniform small grainy structure suitable for further heat treatment in order to use them as metallic matrixes of composite materials are adduced.

The conditions of melt of alloys of a zirconium without oxidation and gas saturation are determinate, the sources of contamination of metal and role of the factors influencing to getting of alloys with the contents of impurity inculcation at a level less than  $0,1\%$  are investigated. The influence of the different factors on degassing of metal at melting is investigated.

The results melting refining of scraps of a zirconium alloy Zn-1%Nb in vacuum  $10^{-4}$  MPa, at power 20 kW/kg, time refining 60-90 s and intensive electromagnetic intermixing of a melt are adduced. The contents of oxygen in storage has decreased from 0,15- 0,2 % up to 0,07-0,09%.

The modeling of a thermal mode of crystallization of zirconium storages in copper and combination metallic chills is conducted. The conditions are investigated, at which the refinement of a cast structure of storages, increase them homogeneity and decreasing casting defects of storage is achieved.

## **DISPERSION-STRENGTHENED FERRITIC STEELS AS FAST-REACTOR STRUCTURAL MATERIALS**

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The ferritic steels are the most perspective structural materials of the hot zone of fast nuclear reactors. However their high-temperature strength is not enough for the work at the planned temperature (700°C). The main results of development of powder steels strengthened with titanium and yttrium oxides are described in this report.

The investigation of mechanical properties in the temperature range -196 - +700°C and creep resistance at 700°C have shown that the steel with 3%  $Y_2O_3$  have the most higher properties. The transposition of the obtained results to 10000-hours give creep resistance 70-90 MPa.

For the determination of irradiation resistance the DS-steels have been irradiated in the WWR-M and BN-600 reactors and in high-energy-ions accelerator. The swelling DS steels doesn't exceed 0.25% by the fluence  $2.6 \times 10^{23}$  n/sm<sup>2</sup>, the ductility after this fluence is 3-4%. The embrittlement DS steels doesn't observe by all investigated conditions. The achieved properties are the best among known ferritic steels.

One of the main causes for structural material fracture' in the hot zone of fast reactors are the different kind of corrosion. The most dangerous corrosion are liquid metal embrittlement and material fracture due to interaction with Cs and Te. The study devoted to corrosion resistance of DS steels in liquid Li and Li-Pb eutectics and low frequency fatigue in eutectics was made. Both corrosion resistance and low frequency fatigue DS steels are on level of steel 10Cr12WNbVB which is the most of corrosion resistance from ferritic steels. The investigation of corrosion of DS steels by interaction with Cs and Te vapors have shown that they have higher resistance and they are the most promising steels for the fast reactor hot zone.

The analysis of received results allows to draw a conclusion that the developed DS steels meet the main requirements for the structural materials of the hot zone of fast nuclear reactors.



STRUCTURE, PHASE AND CHEMICAL STRUCTURE OF THE  
SPRAYED POWDERS OF AN ALLOY Ni-Mn FOR SYNTHESIS OF  
DIAMONDS.

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Are investigated structure, phase and chemical structure of powders of an alloy Ni-Mn, received by turning of an merged, and also centrifugal dispersion in environment of a mix Ar and nitrogen at speeds of cooling  $10^3$  -  $10^8$  C/s and containing various quantity of carbon (0,05 mas. % and 1,13 mas. %).

On the data of the metallographic researches with the help microscope "Neofot-21" structure of a shaving with the contents 1,13 mas. % With is characterized by presence large (up to 0.1 mm) carbids, insignificant sites of a firm solution Ni-Mn-C of the dendrits form and eutectiks. The powders sprayed at speed of cooling  $10^3$  -  $10^4$  C/s, have the dendrits ultrasmaalldispersive structure, and the increase of speed of cooling up to  $10^6$  C/s and above results in homogenization of a firm solution and occurrence with the equailly axis of grains by the size 5 - 8 microns in which are available of the ultrasmaalldispersive carbids inclusion by the size up to 2 microns. In an alloy with the contents of carbon up to 0,05 mas. % are observed dendrits of a firm solution between which grains there is a phase intermetallics Ni-Mn with the size no more than 15 microns.

The researches of phase structure of alloys have shown presence in an small carbon-alloy only of firm solution on a basis  $\gamma$  - Mn, of carbids manganese  $Mn_7C_3$  and Ni-Mn intermetallics. In the sprayed powders ultrasmaalldispersive carbids of allocation in regular intervals are distributed on all structure and, thus, all structure represents kvasievtectics, that allows to assume an opportunity the melt of an alloy during synthesis of diamonds.

By study with the help of a neutron activity method of presence in an alloy of impurity of oxygen and nitrogen is established, that the shaving has the increased contents of oxygen of the alloy, dissolved during preparation, and its crushing by turning processing. At dispersion occurs of the refine powders from impurity of oxygen, and the contents of nitrogen in powders of the cooling, received at speeds, up to  $10^4$  C/s is higher, than in an initial alloy for the account at saturation them from gas environment in which the dispersion is carried out. At the same time increase of speed of cooling up to  $10^3$  -  $10^8$  C/s results to of the refine powders from all harmful impurity.

THE STRENGTH OF REINFORCING FIBRES FROM Nb-Ti  
ALLOY AT HIGH PLASTIC DEFORMATIONS  
IN COMPOSITE WITH METAL MATRIX

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The paper deals with the investigation of titanium-niobium alloy (NT-50) hardening depending on the change of its structure, namely, the change of crystal lattice parameter ( $a$ ), size of mosaic blocks ( $D_0$ ), value of lattice microdeformation ( $\Delta a/a$ ), quantity, amount and density of second-phase precipitation ( $n_l$ ,  $D_l$ ,  $N_l$ ) initiated by high plastic deformation. The niobium-titanium alloy fibres of 3000 to 0,05 m diameter have been investigated after a preliminary etching from the composite deformed with the total extrusion  $\sim 10^3 \cdot 10^{12}$ .

It is found that fibre strength can approximate the theoretical value due to a significant deformation hardening. For a 6 m-diameter fibre the average value strength (extrusion of  $2,25 \cdot 10^8$ ) is equal to 1620 MPa and the theoretical strength estimated by Cottrell approximately equals 2000 MPa.

The analysis of the character of the statistical distribution of the micrometer-section fibre strength evidences that nearly 74 % of all the values measured differ from the rupture-strength average value for less than the standard deviation value.

### EFFECT OF IMPURITIES OF 3D-TRANSITION METALS ON THE OPTICAL PROPERTIES AND ELECTRONIC STRUCTURE OF COPPER

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Such transition metals as Fe, Co and Cr poorly dissolve in copper so that the limiting solubility at room temperature, according to the literature, does not exceed 1%. Consequently, the optical characteristics of the Cu-Fe, Cu-Co and Cu-Cr alloys at a fixed wavelength, namely, refraction  $n$  and absorption  $\kappa$  indices as well as reflection coefficient  $R$  are expected to be linear functions of impurity concentration. However, the optical studies on these alloys have shown that the linearity of optical characteristics holds true at much higher impurity concentrations  $C > 10\%$ .

As source data, the results of studies of the optical properties of Cu-Fe, Cu-Co and Cu-Cr alloys measured within a wide spectral range from 0.25 to 1.25  $\mu\text{m}$  (1.0 to 4.9 eV) and calculated from them electronic structures of the alloys with impurity concentration up to 40% were used. It is shown that, at concentrations  $C < 10\%$ , the optical characteristics are nonlinear, which is due to a complex rearrangement of the Cu electronic spectrum in adding Fe, Co or Cr. It is established that at these concentrations the impurity bands are formed in the solvent electronic spectrum, located between the top of the d-band of Cu and the Fermi level. The presence of this band results in considerable changes in the optical properties of the above materials at low photon energies  $< 1.5$  eV at small additions (up to 10%) of 3d-transition metals. At the energies of 1.5 to 4.9 eV, the optical properties of the alloys are similar to those of copper and this fact means that the copper d-bands, which are responsible for the complex behaviour of the optical properties dispersion at the indicated energies, remain almost undeformed and the impurities, as already mentioned, form the localized d-bands 1.0 to 1.6 eV below the Fermi level.

It is shown that at high impurity concentrations  $C > 10\%$  the alloys are a heterogeneous mixture of nearly pure Fe, Co or Cr and a Cu-based solid solution containing approximately 95% of Cu. The experimental dependences of the optical characteristics  $n$ ,  $\kappa$  and  $R$  on the wavelength are formed as a superposition of respective Fe, Co or Cr spectra and the mentioned solid solution with corresponding weights.

## THE PECULIARITIES OF AMORPHOUS IRON-BASE HIGH ALLOYS AFTER QUENCHING OF MELT

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Potentials of operational features increase of iron-base materials with high physical-chemical properties for reinforcement of constructive articles obtained on the base of traditional technologies to a certain extent have been exhausted, as they are bounded by properties level of the material in use. That causes the necessity of engineering and application of non-traditional processes for alloy treatment both in solid state and in the liquid one. Specifically, among them is melt quenching.

Both the interrelation of structure and mechanical properties of amorphous iron-base high alloys in the course of their melt quenching and their structural features during isothermal annealing were under investigation.

Close arrangement and also its topographical and chemical components were demonstrated to be of first importance in understanding of atomic structure during alloyage. As this takes place, the strong inter-atomic interaction between heterogeneous atoms takes a deciding part in amorphous structure formation.

During amorphization the ordered masses of atoms with high packing density are formed. In other words, both solid solutions of implantation and replacement and also amorphous phases of Me-Me-like are formed. Of great importance, in the ratio of atomic radius of the component and melts overcooling, moreover the over saturated solutions are formed immediately from the melt. The formation of amorphous phase according to Me-Me as a result of melt quenching rate is an order of magnitude greater of  $\alpha$ -phase hardness value, of which the last one is formed and also abrupt increase of its strength.

Widening the scope of solid solution during quenching of iron-base high alloys with eutectic constitution tends to strongly change of structure increasing contamination of alloying elements and amorphous phases according to Me-Me in datum "cluster" that affords to sudden increase of mechanical properties of the alloys. With a rise of melt overcooling the degree of close arrangement and maximum in curve of concentration dependence of enthalpy of combination formation of stoichiometrical composition is particularly pronounced.

### SINTERING OF PERMEABLE MATERIAL ON THE BASE OF BINDED GAUZES

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Porous gauze materials (PGM) are widely used to produce filtering elements, used for purification of liquids, gases, polymer melts. Effectiveness of using filtering elements on the base of PGM is determined by the structure of its porous space.

Improving the main physical-mechanical and hydraulic PGM properties is possible due to making inhomogeneous porous structures of various kinds. In this connection making multilayer composites from dispersive components which differ in its shape and grading are promising.

A technological scheme of fabricating PGM composites includes: cloth binding, location and spacing of blanks, forming of bags from gauze and powder, their densification with further sintering.

The bags sintering (a source material-wire from corrosion resistant steel of austenitic class X18H9TBI, diameter - 55  $\mu\text{m}$  and the powder IIX18H9 with particle size (-40+55)  $\mu\text{m}$ ) was made in a vacuum furnace of CHBЭ-1.3 type in the temperature range 1200-1250°C. Comparative metallographic analysis showed that the process of PGM sintering is accompanied by melting of the source fibers along the grains boundary, by decreasing of the content of the main alloying elements and of the material corrosion resistance.

High specific surface of the IIX18H9T powder made by a method of joint reduction with a calcium hydrate of oxide mixtures with metal powders enables to stabilize a chemical composition of the gauze material during sintering, preserving it on the initial level as well as to achieve lowering the temperature of composite sintering in the average on 100-120°C as compared with PGM.

Therewith it is expedient to use step by step heating with preliminary exposure under  $T=950-1000^\circ\text{C}$  within 1 hour that enables to achieve equalization of the chemical composition of the powder and the fibers as well as to increase corrosive properties of the permeable material.

## DEVELOPMENT OF A TECHNOLOGY OF REMOVING Al, Ca and Si IMPURITIES FROM COPPER-PHOSPHORUS ALLOYS

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The currently employed method of industrial production of Cu-P alloys is based on introducing solid phosphorus into molten copper [1]. The drawback to this method is the necessity of using red phosphorus, which is an expensive and environmentally hazardous product. Moreover, a significant portion of the phosphorus is lost in the process as vapours, which results in extra expenses on cleaning the environment.

We have suggested an economical and environmentally clean aluminothermic method of producing copper with phosphorus alloys, wherein the source of phosphorus is apatite concentrate [2]. The crude alloys obtained by this method contain impurities of aluminium, calcium and silicon in quantities exceeding those given in All-Union State Standard 4515-81. The impurities in these alloys are mostly present in the form of phosphides and oxides of the above elements. The development of the adaptable to streamlined production techniques of removing the impurities from the alloy was the aim of this work.

By using thermodynamic calculations the possibility of refining the alloy from the impurities was shown and experimentally tested by three methods:

- introducing of fluxes and polytetrafluoroethylene into the alloy;
- introducing fluxes and water steam;
- introducing fluoroapatite.

The most efficient and easily reproducible method that using fluoroapatite. The regularities of the process of refining have been studied. It is shown that the temperature of the process of refining should not exceed that of decomposition of  $\text{Cu}_3\text{P}$  - the main component of the copper-phosphorus alloy. The behaviour of phosphorus and the impurities in the melt has been studied. The dependence between the desired degree of the alloy purification and the necessary for the refining quantity of fluoroapatite has been established. A method of conducting the processes of producing and refining of the alloy in one reacting volume has been suggested and realized.

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**INFLUENCE OF THE ADDITION OF SCANDIUM AND OTHER  
TRANSITION METALS ON THE STRUCTURE AND  
MECHANICAL PROPERTIES OF ALUMINIUM-MAGNESIUM  
ALLOYS AND THEIR WELDED JOINTS**

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The last decade is characterized by a sharp increase of production and using of aluminium alloys in various branches of engineering. Traditional methods of increasing the complex of physical and mechanical properties of aluminium alloys (strength, plasticity, weldability, high-temperature strength, fatigue strength, corrosion resistance) are practically exhausted, but modern engineering requires simultaneous increasing the whole complex of properties. Aluminium-magnesium alloys have high plasticity, good corrosion resistance and weldability in comparison to other types of aluminium alloys. However, their strength is lower than in a number of other aluminium alloys. Theoretical and experimental premises testify to the possibility of a significant increase of strength and other characteristics of aluminium-magnesium alloys on account of alloying by small additions of scandium.

Thus, positive influence of scandium and other transition metals on the properties of aluminium-magnesium alloys is very interesting and practically important.

In the presented report there are given the results of studying the influence of additions of scandium and other transition metals on hardness, mechanical properties (strength, plasticity) and structure of aluminium-magnesium alloys and their welded joints.

Investigation were made for alloys in as-cast state, after various kinds of deformation (extrusion, rolling) and conditions of thermomechanical treatment. The alloying of aluminium-magnesium alloys by scandium and other transition metals (Zr, Mn et al.) is shown to cause the growth of strength and hardness of the base metal and welded joints. The recrystallization temperature of dispersly hardened aluminium-magnesium alloys with scandium and other transition metals appeared to be close to the temperature of their melting.

**SEMINAR G.  
COMPOSITES WITH THE CARBON MATRIX**

**214-239**



## NEW THERMOELASTOPLASTICS: PROPERTIES, TECHNOLOGY, APPLICATION

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New thermoelastoplastics based on chlorvinyl polymers (CVP) and polyurethane elastomers (PU) have been developed. Formation of physical network between elastomer and glassy polymer in present system occurs due to specific intermolecular interactions. Peculiarities of physical network formation depending on CVP nature (polyvinyl chloride, perchlorvinyl resin, chlorvinyle vinylacetate and chlorvinyle vinylidene chloride copolymers), concentration and nature of polar groups in PU, components ratio, and also physico-mechanical properties of composites were studied. It was shown, that strength of materials corresponds to the additive values or exceeds them due to polymer-polymer complex formation. Composites have one glass-transition temperature which is regulated in wide range by ration of polymer and lowmolecular mass plastificaters. At 30-40% PU content thermoelastoplastics on main mechanical parameters ( $G=40-60$  MPa,  $E=3-8$  MPa,  $\epsilon=400-700\%$ , residual deformation 0-20%, resistance to multiple bending more than 1000 thousand cycles) do not yield to segmented polyurethanes (SPU), and in resistance to hydrolysis, atmosphere resistance, oil-resistance, incombustibility overcome SPU. Apart from, they are cheaper substitutes of SPU.

Developed thermoelastoplastics are processed from powdery compositions by means of forge-rolling and extrusion in temperature range 140-175°C, or by dissolving technology using dimethylformamide, ethyl acetate, ethyl methyl ketone, acetone etc. as organic solvents.

Prospect of production of high-strength films and doubling different materials by means of solvent-free harmless technology. It was also shown the possibility of using those materials as coatings, glues, synthetic skin having wide range of properties, which can be applied at different branches of industry.

## METALLICONTAINING POLYURETHANES

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Modification of hydrazinecontaining-polyurethanes by complex-formation with polyvalent metal of variable valency [1-2] is perspective method of improvement separate properties of hydrazinecontaining polyurethanes.

It was investigation modification of polyurethanesemicarbazides(PUS) by metal salts:  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Cd}(\text{CH}_3\text{COO})_2$ . Coordination with atoms of metals according to IR- and UV-spectroscopy data is realized by macroligands of macrochain with formation macromolecular metalocomplex by means of both intermolecular and intramolecular coordination [3]. Investigation of obtained polymers is evidence about intermolecular coordination, accompanied by increasing of polymer's firmness and decreasing of its solubility.

Physico-mechanical investigations were shown extremal character metallicontaining PUS from natural and quality of metal salts in polymer. Indexes of firmness polymer increas on 20-60% against with initial ones when took place the interaction of active groups in macromolecule. It was shown by SAXS method that addition 0.2- 0.4 mole  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (on one mole dihydrazide fragment) to PUS the reinforce of segregation of hard and soft blocks and increasing of maximum polymer's firmness, as result.

It was shown that investigation of thermostability (240 h, 353K) of metallicontaining PUS  $K_g$  was 0.9-0.99 and 0.7 for initial polymer. Chelat-containing PUS have the more high termo- and hydrolytic stability and resistance to photodestruction in comparision with basic material.

Afore – named metallicontaining polyurethanes can be used in machineconstruction as lacquer base for priming and coloured compositions, whith should be protect against corrosion.

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# NEW COMPOSITIONAL POLYURETHANE MATERIALS ON THE BASIS METALLOCHELATE AZAMACROCYCLIC COMPLEXES

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Ion - selective polymers are the potential candidates for converting of "wet" ionic devices in "dry". It was suggested, that the ion - selective transport should be carried out by the relevant architecture of a polymeric matrix [1,2]. The present report is bound to design of polyurethane's materials on the basis azamacrocyclic complexes of copper and nickel, which are materials with potential single-ionic (anionic) conductance. The polymeric materials were synthesized on the basis of poly(oxytetramethylene glucol), (molar mass 1000 g/mol), 4,4'-methylenebis(phenyl isocyanate) and azamacrocyclic complexes of perchlorates Cu(II) and Ni(II), 3,10 - (2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane, included in the main macrochain.

We investigated an electrical properties, relationships between structure and morphology on the one hand and molecular mobility on other hand in polyurethane materials with metallochelate azamacrocyclic complexes of copper and nickel in the main chain. The above-mentioned materials have been investigated by means of small-angle X-ray scattering, differential scanning calorimetry, broadband dielectric relaxation spectroscopy (from 0,01 Hz to 1 GHz at temperature from 253 to 313 K), thermally stimulated depolarization currents and sorption of water.

Explored compositional polyurethane's materials are characterized by a dimensional macrolattice appreciably uniform on the size of hard domains. The structure of a polymeric chain influences a dispersion of the sizes of hard domains, density of packing in domains, the degree of microphase segregation (the value of latter in afore-cited compositional polyurethane metallochelates was much higher in comparison with well-known polymers of an ionic type).

The differential solution heats are confirmed, that in viewed compositional systems the substantial portion of soft chain segments of a matrix is immobilized sterically at the interfaces with the hard chain segments of microdomains. The polymers are characterized by low temperature of a glass transition, high melting point of the hard segments of microdomains, high value DC of electrical conductivity and low value of a relaxation.

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# DEVELOPMENT AND RESEARCH OF POLYFUNCTIONAL HEAT PROTECTIVE COATING.

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High requirements to the construction of carrier rocket as far as weight expenditures concerned put tasks on further improvement of thermo protective materials. Besides that to this class of materials not only requirements for ensuring thermic regime of constructions during aero-dynamic heating are applied but also during affect of other highly energetic flows.

Constructions of polyfunctional thermatic protection consisting of several materials and ensuring resistance at weight expenditures  $\sim 6$  kg/sq.m are known.

In order to reduce weight expenditures to  $\sim 3.5$  kg/sq.m and quantity of materials in the construction of polyfunctional protection, the monocoating type Stivlon has been developed on the basis of thermoresistance silicon and specially made empty tungsten glass spheres. A number of analysis and experimental research has been held and it has been proved that the coating with nominal thickness  $\sim 4.5 - 5.0$  mm ensures reliable protection of the construction against joint affect of highly energetic flows of the required power and aerodynamic heating.

Technological regimes of applying and drying of coating on big sized surfaces ensuring high adhesion strength with constructional materials have been worked out.

# STUDY OF PROCESSING PROCESS OF THE REINFORCED POLYACETALS

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The reinforced polyacetals (copolymers of 1,3,5-trioxane) have high durability, rigidity increased heat resistance and wear intensity, low factor of friction. For want of manufacturing of items from data's of aggregates the incorrect choice of technological parameters of molding under pressure can reduce in aggravation of their mechanical properties because of a possible destruction of polymer and unfavorable conditions it of a crystallization.

We investigate process of processing of copolymer STD-B, reinforced by carbon and basalt filaments. Is established, that in the field of high voltages of a shift the velocity of a shift of basalt-plastics (as against carbon-plastics) considerably depends on temperature, that allows to increase productivity of process of molding under pressure of basalt-plastics by magnification of temperature of the material cylinder. The upper bound of temperature of molding (220 °C) is limited to an acceleration of process of a thermal distraction of a polymeric matrix. The increase of pressure of molding up to 70 % from maximum pressure developed molding machine, results in significant increase of mechanical properties an angle both basalt-plastics and decrease of a shrinkage of finished products. The weak dependence of mechanical properties of aggregates on temperature of the molding form is established.

Thus, investigating reological properties and optimizing technological parameters of process of processing of the reinforced polyacetals, is reached significant (up to 40 %) increase of their physical-mechanical properties, that will allow to reduce a mass of constructions from polymeric aggregates at the expense of deriving qualitative items.

**CHARACTERISTIC PROPERTIES OF COATING  
MANUFACTURING METHOD OF POLYMERIC COMPOSITE  
MATERIALS**

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Polymeric compositions have one important characteristic property which lies in the fact that the material and structure are formed simultaneously during manufacturing process, and a quality of the material obtained and structure serviceability in general depend on the technological process quality.

The quality and functional properties depend mainly on type of filler, binder, their interaction behaviour, deposition method, forming and curing mode.

During researches main rules were established to provide under production conditions the specified physical-mechanical, thermal-physical and special characteristics of multifunctional thermal-protective coatings (MFTPC).

A development of the manufacturing method and equipment complex for programmed coating winding on the basis of various filler compositions of asbestos, silica, quartz, carbon, hybrid filaments and matrix of phenolic-formaldehyde type oligomers and thermoplastic materials was a critical moment in MFTPC production; with that an ability was provided for integrated mechanization of basic technological operations.

A set of researches on using the various coating formation methods was performed.

A new method of sequential layer-by-layer coating formation was proposed and investigated; it substantially reduced the power consumption and manufacturing labour input.

It was established that a preliminary binder magnetic treatment causes a more stringent ordering of the oligomer net-shaped structure, stabilization of mechanical characteristics.

A new design-and-manufacturing solution to form the coating thicknesses varying in axial and radial directions at expense of integration of winding operations and programmed shaped prepreg cutting was proposed.

MFTPC (multifunctional thermal-protective coatings) developed and manufactured were tested, certified and introduced into construction of upper parts of various purpose products.

The equipment developed has a number of operational, ergonomic and economic advantages in comparison with known ones.

## ORGANIC-MINERAL POLYMER SYSTEMS

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The results are presented of study of organic-mineral systems (OMPS) formation physic chemical peculiarities. The OMPS are based on silicates water solution, isocyanate contained compounds and various reactive monomers or oligomers (oligo acrylate ester, epoxy)

The structure of number of silicates was analyzed. It was shown that silicate-anion when situated in water solution is partially dissociated, hydrolyzed and is included in chemical structures of different molecular weight (MW). The mean value of the liquid glass anion MW regularly decreases from Li(H) to K anions in the Li(H),Na,K row. The cation size, the rate of positive charge screening, the ability of silicate to dissociation are increasing in that row

The possibility was shown for silicates to initiate the organic component of OMPS polymerization. That determines the next stages of OMPS formation [1].

The organic-mineral products with interpenetrating polymer matrices - silicate and organic were obtained during joint polymerization of liquid glass with epoxy and isocyanate oligomers. It was found that these two matrices are bound due to the formation of silica organic urethane [2].

The mechanism is proposed of inverse emulsion of such systems stabilization due to the amphiphile compounds formation. That can be the main reason to phases inversion.

The evolution of the chemical transformations in OMPS was analyzed in accordance with their phase content changes.

Using the OMPS developed the polymer composites were obtained of high physic-mechanical characteristics, chemical and radiation stable. These composites are applied as adhesives, concrete hermetic coatings, polymer binders for building materials and environmentally safe pressed wares using wood- and agriculture industries wastes (sawdust, stems etc.)

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## CONDUCTING COMPOSITES: SYNTHESIS OF POLYANILINE ON POLYURETHANE MATRICES

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The use of segmented polyurethanes (SPU) as a matrix for synthesis of polyaniline (PAn) allows to prepare highly efficient conducting up-to-date composites for electrotechnical industry. The synthesis was carried out by the way of chemically initiated polymerization in the presence of SPU powders of a various structure in the ratio SPU:PAn = 1; 2 and 4. Volt-ampere characteristic (VAC) of the composites were measured at 293K in the voltage range 0 - 0,1V and 0 - 1V. It has allowed to study the display electronic traps of various depth and their influence on the VAC curve configuration. It is linear for initial PAn, i.e. its shape follows Ohm's law. The VAC curves of PAn-SPU composites are described by Child's law and have the form, characteristic for the processes with the existence of saturation current. The presence of knee points on the curves indicates the transition to the condition of gradual filling of traps. From here it is possible to make a conclusion that SPU in the structure of the composite not only creates the traps for free electrons, but also keeps them there. The presence of hysteresis on the change of current curves testifies to stability of keeping when cyclic changing of the voltage. To all samples of composites the higher magnitudes of a current for identical values of the voltage are peculiar when its reversing. As for initial PAn the linear dependence of a current is characteristic with cyclic change of the voltage in the range 0-1V, the keeping of electrons current in traps, created by polyurethanes gives composites new properties of accumulation and preservation of a charge, i.e. properties of electret. The results of research have shown, that the composites do not lose the basic property of polyaniline - the conductivity, however the interaction of PAn with polyurethane matrices results in occurrence of properties, new, unusual for initial polymers.

The results of thermomechanical analysis allow to assert, that PAn plays a part of active filler, and the plasticity of a the composite grows with the increase of the matrix contents. The increase of polarity of rigid blocks and, as a consequence, the strengthening of interaction of components results in formation of steady physical bonds between PAn and rigid domains. Thus the temperature of viscous current of the SPU sample raises from 473 up to 515K in its composition with PAn. Thus, the composites on SPU-matrices get the technological effectiveness and the ability to processing unusual for individual PAn.



### COMPOSITE MATERIALS, BASED ON COMPLEX DERIVATIVES OF METALS

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Amine and oxyhinoline complex derivatives of copper, nickel, iron, chromium, aluminium were used as active fillers for obtaining of abrasive composite materials on the basis of diverse monomeric and oligomeric binders.

The temperature in the grinding zone essentially exceeds the limits of thermal stability of used compounds. Correspondingly, in process of functioning they are subjected to thermal degradation. It was found that ultradisperse metal particles, formed as a result of degradation of complex compounds, are able to dope the surface layers of the machined materials.

Using complex derivatives instead of salts of organic acids (for example, carboxylates) makes it possible to form in grinding zone the ultradisperse metal particles in thermodynamically active state.

Size, form and structure of such particles are connected with the type of complex compound, the nature of polymeric matrix and the conditions in grinding zone. Using of oxyhinoline complex derivatives makes it possible to obtain in elementary form some metals, which can be got only in the form of oxides if produced by degradation of amine complexes (in particular - iron and chromium). It becomes possible at presence of substances, able to emit substantial quantities of free radicals in process of decomposition. The combination of the deficit of oxygen in contact zone with high concentration of free radicals, produced by polymeric matrix in process of degradation provides favorable conditions for the formation of active ultradisperse metal particles.

Surfaces of metals and alloys, doped in process of grinding, demonstrate increased level of their functional properties.

# MICROELECTRICAL SENSORS FOR SELF-INFORMING POLYMER LAMINATE COMPOSITE BLANK AND FINAL PARTS

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Critical problems of polymer composite large sized part manufacture and use are concerned with providing the polymer matrix state monitoring in blank parts during manufacturing processes and at the same way in final parts during their operation to evaluate and/or predict kinetics and degree of matrix chemical and physical transformations in the processes and the operation.

One way to solve the problems is to develop microsensors that can be placed directly at points in or on a laminate composite part where processing or aging data are required and can keep up their serviceability in the final part. A complex microelectrical sensor is developed that is made on an integral film base and consists of microdielectrical gauge, capacitance type pressure cell, tensometric transducer as well as temperature detector.

This paper describes results received by using the complex microelectrical sensors to study curing process of a model epoxy resin and polymer laminate composite and physical and chemical changes occurred in the cured systems due to thermocycling, sorption of polar solvents and mechanical loading.

## INTRODUCTION OF PREPREG TECHNOLOGY FOR MANUFACTURING OF COMPOSITES

L.G. Kovalenko

The purpose and the problems of this work were the replacement of the technology of "wet" impregnation of glass-fibre fillers by epoxy linkings for the production of sports goods from wood by "dry" impregnation technology.

Introduction of preprag technology was conditioned by such advantages as in the process of composites manufacturing: considerable reducing of materials and power resources consumption, and improvement of staffs conditions of work.

Issuing from the criterion of ensuring of composites maximum firmness the linkings on the basis of epoxy resins aromatic amines.

Were developed some marks of epoxy-amines preprags viable at temperature of  $20 \pm 2^\circ\text{C}$  during 2 days. By preprags storage in premises with temperature  $0 \pm 5^\circ\text{C}$  their stability raises to 18 days.

By manufacturing wood layer plastic preprag layers alternated with wood layers.

The conducted researches showed that the developed compositions provide not only equal firmness of glue connection with stuck wood but also raise adhesion firmness and hardness of a layer plastic.

Composites developed with using of preprags had higher firmness indices than those which were on the basis of unreinforced layer stuck wood. For example, plastic on the basis of a birch veneer and a glass-fiber epoxy-amines preprag have firmness indices on 15-80% higher than the specimens having a stuck birch basis.

Pressing time of a layer plastic it was succeeded in reducing it in 3-4 times.

Service term of sports goods (hockey sticks, skis, bows, rackets, etc), reinforced by glass-fibre preprags raises 2-fold or more in comparison with pure-wooden preprags (firmness and water stability raise).

Preprag technology effectiveness at manufacturing of carbonic plastics was determined by the author too.

**INFLUENCE OF THE COMPONENTS RATIO ON THE  
ADSORPTION OF THE POLYMER MIXTURES UNDER PHASE  
SEPARATION OF SOLUTIONS**

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An influence of the components ratio on the polymer mixtures adsorption in the two phase condition was estimated. Transition toward the two-phase condition was attained by the increasing of the solution concentration up to the phase separation. For solutions that have separated into two phases with increasing component concentration, the adsorption from each phase has been studied separately and the total adsorption from two phases has been calculated.

The polystyrene-poly (butyl methacrylate)-CCl<sub>4</sub> system was investigated using fumed silica as adsorbent. Simultaneously the fraction of segments of each type immobilized by the surface was determined from NMR spectra. In all cases, poly (butyl methacrylate) is characterized by preferential adsorption.

The main features of adsorption are similar in both one-phase and two-phase states; however, the values of adsorption and fraction of immobilized segments are different for adsorption from two separated phases because of the difference in the ratio of components and their concentration in each phase. The distinctions in adsorption from one-phase solutions before phase separation and from solutions modeling separated phases are connected with redistribution of components between upper and lower phases. As the result, their ratio does not correspond to the initial ratio and therefore thermodynamic conditions of solutions, responsible for adsorption, are changed. Because of it, the shape of isotherms of adsorption and adsorption values are determined by the different level of aggregation in solutions with various ratio of components.

**THERMOSTABLE COMPOSITE MATERIALS FOR THIN-  
WALLED ELECTRICAL HEATERS.  
THERMAL CHARACTERISTICS**

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The electrical thin-walled heaters have been developed to use them for heating and warming of components of various mechanisms and equipment operating under negative-temperature, roads, buildings, dwellings and service rooms. The heater is the plate 2 to 5mm thick with up to 2x2m (length) x (width). The heater characteristics are as follows: supply voltage 1 to 500V, direct or alternating current, allowable temperature value in interval of 80 - 300° C. Power density depends on temperature value allowed and heat removing intensity and it is equal to 0,1 - 10 kWt/m<sup>2</sup>. The non-metallic current carrier (organic conductor) is used. The heater material density is about 1,1 - 1,7 g/cm<sup>3</sup>. The heaters could be formed on rigid or flexible frame. In the last case the heaters are suitable for heating driver's cab sitting and floor in automobiles and buses.

The heaters were made using four developed isocyanate based polymer thermostable binders of various type: liquid or powder-like, both cold- (20 - 30° C) and thermo- (150 - 200° C) curable.

The electrical insulating thermostable composite polymer materials were obtained, with degradation beginning at 300 - 350° C and maximum rate of degradation in region of 550 - 600° C. The electric disruption strength exceed 2,5 kV at normal conditions.

The developed thin-walled heaters can be used for:

- heating of cabs and rooms ( for example operator's cabin in outdoor working machine, bus or train coupe, dwellings or service room etc.);
- technological liquids frizzing prevention in volumes and tubing under 0° C;
- heating and warming of machinery and equipment that operate under conditions of processing and manufacturing schemes;
- the soil and mining rocks freezing protection.

### Filmy Filled Piezocomposites Based on PVA and PVDF

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The polymer filled piezocomposites are interested for researches and practical persons. It possesses high sensitivity, elasticity and complex-configuration articles can be made from them or filled composites can be used as a coatings.

However, its wide utilization is impeded by an insufficient information about the correlate dependences of a composition, structure and properties of these composites.

The goal of the present work was to examine the influence of the contents of fibrous filler  $\text{LaPb}(\text{ZrTi})\text{O}_3$  in the film composites based on polyvinyl alcohol or polyvinylidene fluoride on structure and electric properties of a composite materials.

The composites were prepared by mixing of 5% of polyvinyl alcohol (PVA) aqueous solution or 9-12% polyformamide solution of polyvinylidene fluoride (PVF) and fibrous powder  $\text{La}_x\text{Pb}_{1-x}(\text{TiZr})\text{O}_3$  (the particles were less 0.5 mm). The fibrous filler content was varied from 30 to 75 mass%. The gradients were carefully mixed, and films were cast over the surface of polished glass. The nickel and nichrome alloy contacts were dusted on films by vacuum thermal deposition technique. The IR spectroscopic, X-ray phase and electronic microscopic methods were adopted to investigate the structure of composite materials. Polarization was conducted in air at the electric field strength of 3-5 Mv/m at temperatures below the Curie point by 15-20°C. Standard industrial equipment was used to measure electric resistivity, dielectric permittivity and loss.

On the base of execute experiment it was established, that additional fibrous filler partially changed a polymer structure and decreased the polarization field strength from 40-100 Mv/m of a pure polymers up to 3-5 Mv/m of the composites. However, this good influence exhibited as filler content increased from 30 to 60 mass%, for all that the value of coercive field was reduced 5-6 times. A further increase of its concentration in composites up to 75 mass% necessiated to elevate the electric field strength. The propose about an interaction of the side polymer groups with oxide fibres and its possible orientation in electric field was made.

## ADHESION STRENGTH OF STRATIFYING POLYMER SYSTEMS

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The reasons of sharp changes of the adhesive characteristics in polymer - polymer systems reached a limit of compatibility are unknown yet. On the one hand, the reasonable explanation of this mechanism can be associated with presence of metastable area in stratifying systems [1]. On the other - with more fundamental processes, for example, with redistribution of intermolecular interactions on binodal when the system is approaching to it from a single phase state [2]. Thermodynamic experiment (the method of a reversed gas chromatography) has shown that the stratification in the systems takes place in a very narrow concentration interval [2,3]. Therefore it was possible to make some conclusions only for a cellulose acetate butyrate - the polyoxymethylene system, namely: the sharp increasing of the adhesive characteristics takes place on binodal, but their drop is observed in a metastable area, which is between binodal and spinodal.

Very fruitful in this respect there was a research of a system copolymer styrene and acrylonitrile - poly(methyl methacrylate) by a dielectric method. It was shown earlier, that the extended areas of compatibility and stratification are characteristic for this system at high temperature. On the other hand, this composition has LCTS, equal approximately 423 K, therefore it would be incorrect to draw conclusions about this system from adhesion strength measurements which were made at room temperatures. The dielectric researches at temperatures 293-423 K have allowed to make a unequivocal conclusion for this system. It coincides with the conclusion for the system of cellulose acetate butyrate - polyoxymethylene.

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MECHANICAL PROPERTIES AND STRUCTURE OF COMPOSITION  
MATERIALS BASED ON FILLED COPOLYMER OF  
FORMALDEHYDE AND DIOXALANE

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Insufficient knowledge of plastifier influence on structure formation of filled crystallizing polymers and its kinetics in particular hinders application of composition materials based on such polymers. Plastifier influence on hypermolecular structure formation and mechanical properties of these materials may result from both increase of macromolecules and their parts moving ability, and ratio change of germ formation rate and development of ordered regions in polymers that. So the aim of this work was study of concentration and molecular mass of polyethyleneglycoles (PEG) influence on structure and properties of materials based on crystallizing polymer - copolymer of formaldehyde and dioxolane (CFD) filled with kaolin or niobium oxide. Optical microscopic, physic-mechanical and calorimetric studies of obtained materials were provided.

It was shown that polymer structure forming in non- isothermal conditions depended on plastifier and filler content. Small addition of PEG with different molecular mass exquisitely decreases spherolyte sizes and makes distribution spectrum of spherolytes dimension more narrow.

It was stated that on rise of plastifier content in filled polymer physic- mechanical characteristics had maximum in region of low content of PEG. Maximal strengthening of composition materials is achieved on certain content of additive and its molecular mass.

The correlation of strong properties of composition materials based on filled CFD with structure change on hypermolecular level was stated. Mechanism of plastifier microadditive action is supposed.

Investigation results are used to elaborate composition materials based on filled CFD with microadditive of plastifiers having notably improved physic- mechanical properties.



POLYMERIC NANOCOMPOSITIONS BASED ON COMPLEXES OF  
POLY(ACRYLIC ACID) WITH METALLIC IONS

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Last years the intensive development of an electron technology has involved a creation of new classes of composite materials – polymere nanocompositions. The similar materials consist of a polymer matrix and filling material as an inorganic component of the colloidal size. The properties nanoparticlas of a disperse phase with the mechanical characteristics of a polymer matrix are combined in a unique way and properties of a such material in many respects differ from polymer compositions mainly filled by large size particles [1]. Obtaining in a polymer matrix the particles of a filling material of so high scales of a degree of dispersion is always hindered by their aggregation. During the interaction of macromolecules with solid particles due to screening of their surface by macromolecules the process of an aggregation of particles is terminated quickly. Therefore, the first nanocompositions were obtained by a complexing of poly(acrylic acid) with Cu ions with further destruction of a complex in presence a filmforminy polymer component [2]. Therefore, there is a process of interactions of polymeric macromolecules with metallic ions in the basis of a creation of polymeric nanocompositions.

For a determination of relations between the nature of polymer and metal with the purpose of creation new nanocompositions with different metals, the researches of a complex-formation between (PAAC) and cations Ni, Co, Fe, Cd in broad concentration and temperature intervals by methods of viscosimetry and IR-spectroscopy were carried out.

The interaction has shown to be carried out between PAAc and cations due to the carboxylic group and according to the stability of complexes PAAc-ion of of metal they can be arranged in following series:  $Cd > Fe > Co > Ni$ , the optimal concentrations of complexing are determined.

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## THE FILMFORMATION OF VINYL OLIGOMER AND ALLYL ETHER COMPOSITIONS

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The production and manufacture of new film-forming substances is essential for technical progress and for the development of paint and varnish industry in Ukraine.

Oligoesteracrylates are almost the only film-forming vinyl substance for this time. Vinyl oligomers are widely used in coats, soaking materials, plastics. We can have the most progressive varieties of the materials for paint and varnish such as oligomer-monomer compositions including the compositions with high dry remainder and the materials of radiation hardening on their basis. At the same time oligoesteracrylates are for from the best types of vinyl oligomers.

The application of oligoesteracrylates is restricted by the relative compleaity of their synthesis, high price, oxygen inhibiting of hardening, not high speed of filmformation during the air drying.

Vinyl oligomers with another (not methacrylic) type of double bonds were not practically used.

We created the new type of polymerizationable oligomers for coats such as vinyl oligoesters which do not yield the oligoesteracrylates as a film-forming substances but for some characteristics (speed of coat forming in the air) surpass them.

The new synthesized vinyl oligoester with the film-forming characteristics – divinyl(bis-o-phthalyl)triethylene glycol (DFT). DFT was synthesized by the method of condensing telomerization from ethylenechlorohydrin, phthalic anhydrite and triethylene glycol. DFT is a viscous yellowish brawn liquid,  $n_D^{20}=1,5363$ ;  $\rho=1259,9 \text{ kg/m}^3$ ; bromine number – 64g Br<sub>2</sub>/100g;  $M=498,49 \text{ g/mole}$ ;  $MRD=127,4 \cdot 106 \text{ m}^3/\text{mole}$ .

DFT compositions with oligomer allyl ether hexaallyl(bispentaerythritesebacinate)diethylene glycol (HASD) give the coats that have a nice decorative qualities. They are transparent and colorless. Films with not more than 80 mkm width get dry very well and do not have a sticky surface ball. The coats are very resistant for the action of intrinsic nonpolar solvents and water but they have a restricted resistant for alkali. The availability of indicated protective and decorative characteristics let us use the compositions of vinyl oligoester and allyl ether as a film-forming substance.

### **ANTIADHESION COMPOSITION COATINGS ON THE BASE OF POLYTETRAFLUOROETHYLENE**

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The purpose this work is elaboration of the antiadhesion coating for details, which is needing to protect from the working product sticking. This problem arises during a packing of products in polymer films on machines. The qualitative packing is arrived in the absence of the products sticking on packing details.

For the antiadhesion protect it is used the polytetrafluoroethylene (PTFE, Teflon) film, impregnated with PTFE fiber glass plastic material, etc. The film is fixed on details by a mechanical way or to stick. These ways are difficultly and don't ensure for the successful long exploitation of details in antiadhesion regime.

In our investigation the antiadhesion composition material was modernized by aluminium oxide and the silicon-organic combination and the technology of coatings on the surface of metal details was elaborated.

Industrial tests were conducted on the milk plant in the packing machine of TETRA PAK.

Results of these tests have shown that the TETRA PAK coating worked 9-15 shifts and the coating of Institute for Problem of Material Science of Ukraine worked till 140 shifts.

## POLYMER COMPOSITE MATERIAL FOR AUTOMOBILE BRAKE SHOES

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Most of the known polymer composite friction materials use the phenol formaldehyde (PFR) and/or epoxy resin or other thermo reacting polymer binders. The PFR based binders can emit noxious compounds (phenol, formaldehyde etc.) during their processing and curing both during friction product forming. Nevertheless these binders are widely used in the brake shoes manufacture.

The friction polymer composition "Polyfrim" is developed consisting of polymer binder, rubber, powdery and fibrous fillers and special additives. Polymer binder include oligoepoxy ether (83 to 96% wgt.), latent curing agent (5 to 16% wgt.) and complex catalyst (0,01 to 1,00% wgt.). The above binder does not give off toxic and ecology dangerous volatile compounds under curing process and improves the thermo-mechanical characteristics of friction material. The binder content in the friction composition is equal to 13,00 - 16,00%. The friction composition can be prepared using the technology existing in industry. The friction composition components are mixed in mixer during 5-10 min. under pressure of 0,6 MPa and temperature below 100°C. The brakes are formed by the friction composition hot molding.

The uncured friction composition has at least 6 month life time. The strength limit of separation from metal frame for thermo treated during 1 hour at 400°C brakes is equal to 6 kN. The same limit of untreated brakes is equal to 27,5 kN. Compare with strength limits of separation from metal frame for PFR brake that are equal to 4,7kN and 12,5 kN for thermotreated and untreated samples correspondingly. The friction composition using the new binder is characterised by absence of noxious gases evolution during operation and decreases environmental pollution.

The optimisation of the fillers relative content and the scheme of curing process allow vary and modify such cured friction composite material parameters as wear coefficient, hardness and solidity, friction coefficient etc.

**PHYSICAL PROPERTIES POLYMER of COMPOSITES.  
RENORMALIZATION GROUP TRANSFORMATION.**

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Researches filled polymeric of composites have shown, that the presence of a firm phase filling is resulted to change of structure supply succession by a polymer, i.e. for physical properties of a composite have an effect not only peculiarity filling, but also its interaction with a matrix (polymer). It much complicates forecasting physical properties polymeric of materials.

With the help renormalization group of transformations in real space structural model of a heterogeneous material is constructed. Modeling stochastic structure a heterogeneous material was spent on the basis of a lattice with casual distribution of its parameters. The units of a lattice simulated heterogeneity (components of system) in space, and connection between units - their contacts with neighbors. The determining influence on maxi-properties heterogeneous material is rendered by conditions contacting between its components, therefore a problem of connections was considered.

In filled polymer materials, part the polymer, being in wall interphase a layer, changes the properties. In such systems conveniently to use a method iterative average (definition of properties of sites breaking). Effective properties polymeric composite of materials, such as thermal conductivity, modules of elasticity and factor of thermal expansion on the base of fractal model of chaotic environment and cell Voronov were determined.

The analysis of influence on effective properties filled polymer materials an aggregatization and clusterization heterogeneous, contact phenomenon between components, linear sizes heterogeneity, percolation of effects is spent. Comparison of accounts with experimental data of physical properties filled polymer of materials was spent which has shown on the good their consent.

**URETHANE-CONTAINING POLYMERIC COMPOSITES BASED  
ON MICROCRYSTALLINE CELLULOSE AND OTHERS  
RENEWABLE MATERIALS**

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Developing of a novel polymeric composites having a regulated physicochemical, mechanical and operating characteristics based on renewable (biodegradable) polymers is of great interest due to increasing requirements for ecological safety and wasteless production of a diverse polymer materials. The research reported shows the method of reactive filling based on preparing of polymeric composite materials by fillers' introduction to source reactive system (mixture) while composite-forming reaction occurred. Urethane-containing and silicone-urethane-containing polymers have been applied as polymer matrices in ionic and non-ionic forms, and as a fillers were used the following natural polymers: microcrystalline cellulose, dextran, and a different types of starch being embedded in polymer matrices range from 10 to 60%. The specimens obtained depending on methods of their synthesis (polyaddition or radical UV-polymerization) exhibit properties both solid films and foamed stuff. The character and type of intermolecular interactions, structural peculiarities and physico-mechanical properties of composites produced have been investigated by IR-spectra, X-ray diffraction analysis and DSC(differential scanning calorimetry) methods. Thermal stability and hydrolytic behaviour in acid and alkaline medium were estimated as well.

It has been shown, that starch and dextran are more "active" fillers compared with microcrystalline cellulose - they change net of hydrogen bonds in polyurethanes and, also hygroscopic water taking part in cross-linking reactions results to forming urea groups in polymeric composites. Compositions obtained while using oligoesters have more biodegradable abilities in the environment than those, which have oligoethers in the flexible (soft) blocks.

The polymeric composites elaborated are of interest as prospective materials for applying as functional polymers for multipurpose applications.

### STRUCTURE AND PROPERTIES OF POLYMER-WOOD MATERIALS BASED ON THE THERMOPLASTIC WASTE

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The polymer-wood material (PWM) is a thermoplastic polymer matrix containing up to 60% by weight of wood cut. Such materials have properties of the both, polymer and wood, and can be processed in goods by typical polymer processing methods, for example, by extrusion or pressing. Obtained materials can be used for manufacturing the packing, furniture, building materials and facing materials. It is a fact of great interest that PWM may be obtained from the polymer waste and therefore it is contribution to very important task of polymer recycling. It makes possible to utilize the thermoplastic waste including mixed one by the way of its joint processing with wood and to produce the new material useful for making goods.

The main purpose of this work was to study how the properties of PWM based on secondary polyethylene (SPE) and polystyrene (SPS), their binary mixtures and grinded wood depend on the PWM composition.

IR spectroscopic studies of virgin and recycled polymers shows that reactive groups have formed in SPE and SPS. Also the wood, on the other hand, can possess active polar groups. Therefore, the components of PWM are capable of specific interaction and hydrogen or chemical bonds formation. As it was shown by calorimetric study these chemical interactions between the polymer matrix, and the wood filler in PWM suppress the development of the supermolecular structure in a crystalline phase of SPE.

Wood filler introduced into the matrix of virgin PE reduces ultimate tensile strength  $\sigma_t$ . At the same time,  $\sigma_t$  increased for PWM based on SPE, indicating that the wood filler reinforces the composite because of the interaction between the filler and polymer matrix of recycled PE. When the polymer matrix is binary blend of SPE and SPS, then mechanical properties of PWC are determined both by interaction of the wood filler with polymer matrix, and by the interaction between its components.

### POLYMEROUS FRICTIONAL COMPOSITION.

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The future of machine construction is connected with the wide use of compositive polymerous frictional materials as they are more technologycal and ecologycal both in their production and application. Asbestos-free polimerous frictional compstions are looked upon as the most advanced materials. While working out new polimerous frictional materials, different filament and thread-like crystals including vollastonite are used to substfitute asbestos. The choice of vollastonite as asbestos substituent is determined by the number of specific properties, such as high heat resistance, arming possibitity and ecologycal harmlessness [1]

The polimerous composition of frictional purpose with vollastonine as a linking filler and modifcator of a non-organic nafure (the natural mineral or synthetic ,made of slag wastes with the help of high-temperature synthesis) was worked out and proved with a patent in The Egoryevsk Technological Institute, named after N. M. Bardigin, MSTU "STANKIN"

The friction tests of the new compositive material were led on the general purpose friction machine MTO-89. The efficiency of braking was checked on the inertia stand, according to the method, prescribed by the UN Economy Comission.

It was found out, that the polymerous compositive frictional material has a stable coefficient of friction of  $0,4 \pm 0,43$ . The general wear nuder the complete sycle of tests results in 0,31 mm.

The efficiency of braking, resulting in the slowing down (under the condition of 100 km/hour, P-5 MPa) is  $6,5 \text{ m/sec}^2$  The efficiency of multiple braking (P-5 MPa, 50 sycles, V from 100 to 50 km/hour) is  $5,5 \text{ m/sec}^2$ . The offered polymerous frictional composition may be used for a wide spectrum of frictional purpose machine parts.



### Electronically properties of the thin organic layers.

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In the last times a considerable interest is shown to the possibility of receiving electronically and optoelectronically devices based on organic structures. It is connect from one side with relatively simple there receiving but from other side with their local electrical connections and strong space nonuniform that is typical for organic molecules. This properties seems useful with tendency of in the microelectronics to go to the region of superlittle size. In this paper will be analyzed the particulars of receiving and electrical properties organic layers that was made from the perylene-3,4,9,10- perylenetetracarboxyl dianhydride (PTCDA), phthalocyanina-Cu- tetera-tetr-butyl-phthalocyanine (CuttbPc), vinylene - poly [2-metoxo, 5- (2'-etyl-hexyloxy)-1,4-phenylene vinylene] (MEH -PPV), oxadiazol derivative (PBD), tris (8-hydroxyquinolinolato-N1,O8) aluminum (Alq).

It is shown that epitaxy and quaziepitaxy layer by layer growth of the organic molecular crystal(OMCs) for example from PTCDA is probable under low velocity of growth (order 1-5 Å/s). A main factor in this process is the temperature of subjects. Under low temperature with geometric order in the same time appear a crossing of orbital along direction of the biggest packing that give us high mobility. By this way was received the mobility of carrier distinguished on 4 order under 90K and under 440K. The carriers mobility is reflect the degree of structural organization and is measured by various methods. As voltage drop in the region of carrier transport for PTCDA or by means of time flying method for Alq. In the first case one mast take in to account potential drop on interface metal current contact- organic film. Difference of electrostatic potentials appear due to the difference of Fermi levels of the thermodynamics phase in contact. One can remove Fermi levels to put a special monolayers between films and subjects. By this way Fermi level 100nm film of MEH-PPV was removed some more 1 eV. Voltage drop on various interfaces borders was measured by Kelvin probe. Sum of voltage drop in the structure that consist of Cu-MEH-PPV-Ca was registered as shift of electroabsorbptions minimum. This minimum appear due to splitting of exciting condition of molecule in the high electric field.

## FERROCENE CONTAINING POLYETHYLENE TEREPHTHALATE

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A synthesis method of polyethylene terephthalate (PET) containing 0,1 -0,5 mol % of ferrocene moieties in a main chain has been elaborated. The synthesis was carried out by usual two-step industrial method: transesterification of the dimethylterephthalate with ethylene glycol in the presence of dimethyl ester 1,1'-ferrocenedicarboxylic acid with required quantities followed by polycondensation of bis-glycolic ester produced [1]. The polycondensation mechanism was studied and the effect of ferrocene units content in a copolymer on the main physico-chemical characteristics of modified PET was established.

It is well-known that the some ferrocene compounds act as UV light absorbents and here found application in stabilizing polymer against the degrading effects of UV light. This method gives a series of advantages compared with the common industrial production method, namely catalysts application are excluded, a polycondensation temperature is reduced and polymer production technological cycle is shortened. The modified PET has stable color (from yellow to brown) and a series of technical valuable properties including higher light resistance. Experimental-industrial batches of film from modified PET having thickness from 12 to 70  $\mu\text{m}$  and ferrocene units content from 0,1 -0,5% mol have been produced on plant «Svema» (Shostka). The films with uniform stable color from light-golden to brown (depending on ferrocene content) were obtained.

Thermal, mechanical and some electrical properties of modified PET films have been investigated by means DSC, TMA, DTMA and electrical relaxation analysis [2]. It has been established that the above properties are dependent on ferrocene units content in PET.

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**SEMINAR H.**  
**COMPOSITES WITH THE POLYMER MATRIX**

**241-258**

### **THERMALLY-EXPANDED GRAPHITE MATRIX COMPOSITE MATERIALS**

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Composite materials (CM) based on thermally expanded graphite (TEG) are promising materials to be used as sealing, heat insulating or friction resistance materials.

Methods and process routes were elaborated in the work aimed at production of TEG-based reinforced materials having elevated mechanical and service properties to replace environmentally dangerous materials of asbestos.

Reinforcing elements in the form of 3-D metallic knitted nets or perforated steel foils when introduced into the TEG matrix, extend the range of mechanical loadings and temperatures and versatility of components made of CM's developed.

The work covers the results of investigations on developing CM with graphite matrix. Various types of reinforcing elements were examined and their structures were optimized according to CM application areas.

The effect peculiarities of structure and volume fraction as well as graphite matrix properties of reinforcing elements on CM's physical/mechanical properties were identified. The introduction of reinforcing elements resulted in ameliorated compression and recovery characteristics, increased compression and tensile strengthes. The SEM analysis has supported a favourable effect of graphite matrix reinforcement with metallic nets. Strength and strain properties of perforated steel tape reinforced materials with TEG matrix were studied in the temperature range of 20 to 600 °C. Service characteristics were determined such as gas permeability and wear resistance for reinforced CM.

RESEARCHES ON THE DEVELOPMENT OF CARBON - CARBON  
HEATERS, CRUCIBLES AND AUXILIARY EQUIPMENT FOR  
MONOCRYSTALS CULTIVATION AND METALS MELTING

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The outcomes of researches on development of heaters, crucibles, thin-walled cylindrical and conic shells, heat shields and other technological equipment for installations of silicon and other semiconducting materials monocrystals cultivation, metals melting and etc. are discussed.

The bars of items are formed by winding of carbon filaments or fabrics on special graphite arbors then using the methods of thermogradient impregnation by the pyrocarbon in a stream of hydrocarbon gas at 800-1500°C. Obtained items were taken away from arbor-heaters, that allows to use them multiply and to have minimum allowance for consequent machining that considerably reduces their cost.

While the crucibles manufacturing in cylindrical or conic carbon - carbon the shells there are inserted graphite or carbon - carbon bottoms. With appropriate choice of CLTE of a bottom and shell materials there are ensured a self-condensation and capsulation of joints while the crucibles heating up to the temperature of metals melting. Crucibles obtained by this way are hermetic even in relation to the silicon melt, do not fail at repeated recurring of a melting-crystallization cycles and cooling up to room the temperature.

The main performances of received materials are discussed. The concrete examples of items by a diameter of 20-700 mm and length up to 1000-2000 mm manufacturing are indicated.

The outcomes of laboratory approbation and industrial tests of items are indicated. Their competitiveness in a comparison with the analogs from industrial graphites is confirmed.

## ORIGIN OF PHASES ON THE BASIS OF FULLEREN IN SYSTEM IRON - CARBON

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The capability of origin of phases on the basis of fulleren in ferrous-carbon alloys obtained from powders mixture of eutectic cast iron and ferro and mixture of powdered iron with 8% fulleren  $C_{60}$  is investigated.

Pressings from mixture of ferro with cast iron heated to temperature, at which the cast iron is melted, and the iron remains in solid state. Samples from mixture of powdered iron and fulleren treated in vacuum by high-current low-voltage microarc operating in rapidly movable microspots.

At heat treatment of samples of systems iron - cast iron in azote and vacuum by X-ray analysis ( $K_{\alpha}$  - Co) the origin of obscure phase with interplanar spacing intervals is revealed: 18,0; 7,09; 4,14; 3,73; 3,56; 2,985; 2,836 and 2,49. The majority of lines can be assigned to the cubical phase with parameter of cell  $a=12,3$  angstrom, the intensive enough line 18,0 angstrom can be examined as superstructural line from planes such as (220) with period of identity, equal quadruple of interplanar spacing interval (diagonal of an edge of unit cell).

It is established, that the heating rate in temperature range 1230-1340 °C exerts influence on quantity of lines from new phase and their intensity on diffractograms.

It is established, that as a result of processing of samples by high-current low-voltage microarc, alongside with fullerene lines  $C_{60}$  on diffractogram there are lines of the same phase with period  $a=12,3$  angstrom, as in the system iron - cast iron.

The phases obtained in experiments on local melting-hardening of cast iron, on visible, represent metallfullerite  $Fe_xC_{60}$ . Fullerene  $C_{60}$  is the steadiest and widespread form fullerene. Therefore is logical to suspect dominance of the form  $C_{60}$  and in melts of cast iron. Besides the fact of obtaining of a similar phase in mixture Fe - 8% $C_{60}$  is padding argument verifying a hypothesis that the FCC phase with parameter  $a = 12,3$  angstroms is folded on the basis of molecules  $C_{60}$ .

## NANOCOMPOSITE OF SUPERCONDUCTING MULTILAYER TUBES IS IDEAL STRUCTURE FOR ABRIKOSOV - JOSEPHSON FLUXONS LATTICE

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In development of the materials science approach to superconductivity problem the creation of novel artificial composite superstructure is suggested, optimized for formation of a mixed Chubnikov phase. Idea is proposed and theoretically substantiated that metal nanotube of  $\approx \xi$  radius ( $\xi$  is a coherent length), surrounded by coaxial-cylindrical layers composed of hard superconductor in kind of multilayer nanotube ("spool"), is ideal and natural trap for pinning of Abrikosov and Josephson fluxons. Coincidence of nanotube cells lattice of  $\approx 4\lambda$  parameter ( $\lambda$  is a depth of field penetration) with fluxons lattice in some magnetic field can result in resonant increase of a critical current  $J_c$  and/or temperature  $T_c$ .

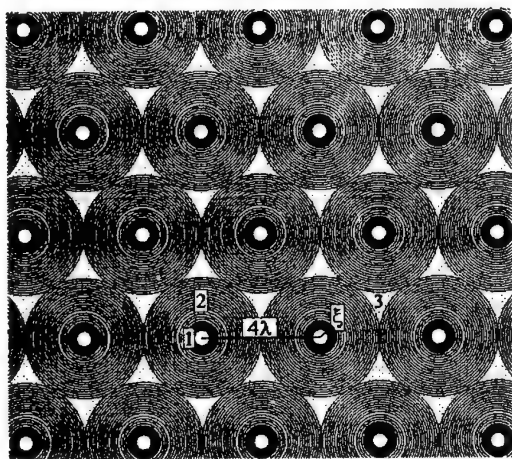


Fig.  
Triangular lattice of nanotube cells ("spools"):  
1 - metal cylinder of  $2\xi$  diameter, in which fluxon core will be formed, the internal surface of which promotes a formation and pinning of fluxon;  
2 - superconducting coaxial-cylindrical shell of  $2\lambda$  thickness, promoting an ideal circulation of fluxon currents;  
3 - Matrix.

To fabricate such a composite the template method can be used. By CVD method the metal tubes are deposited on a polymer membrane containing a pore triangular lattice of  $\approx 2\xi$  diameter and of  $\approx 4\lambda$  interpore distance. After etching, the layered coaxial-cylindrical shells composed of hard superconductor are deposited on tubes brush. The ordering of fluxons and the resonance of the composite geometrical structure with lattice of fluxons, etc., should cause synergistic increase of  $J_c$  and/or  $T_c$ .

# STRUCTURAL AND PHASE TRANSFORMATIONS IN BISMUTH-FULLERITE NANOSYSTEMS

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Metal-fullerite nanosystems are not only new perspective materials with interesting electrical and optical properties, but also convenient object for study of interpartical and interfacial interaction effects due to their structure specificity. In this paper the results of structure and phase composition research of film bismuth- fullerite nanosystems are submitted depending on parameters of the preparation in comparison with pure fullerite films. Bismuth- fullerite nanosystems were obtained by co-deposition in vacuum  $\sim 10^{-3}$  Pa of components evaporated from separate sources on substrates NaCl and mica in the temperature range  $T_s = 300-500$  K at condensation rate 0,25-0,6 nm/s. The concentration Bi ( $C_{Bi}$ ) varied within limits of 0-80,0 at.%. Thicknesses of films was 10,0-100 nm. By electron-optical methods is established that the films on mica with other conditions being equal have higher structural perfection due to closer accordance of the lattice parameters muscovite and  $C_{60}$ . The mechanism and the temperature range of formation of epitaxial films  $C_{60}$  and  $C_{60}$ - Bi are determined. It is revealed that Bi favours to oriented growth of nanosystems reduces epitaxial temperature (up to 433-440 K in comparison with 455-460 K for  $C_{60}$ ) and promotes of formation and stabilization of HCC phase at  $T_s < 470-480$  K.

The experimental data submitted in paper and analysis of the references allow to assert that the final structure of epitaxial  $C_{60}$ -Bi nanosystems is the result of FCC $\rightarrow$ HCC phase transformations proceeding during growth connected with recrystallization and growth of favorably oriented crystals. There is "internal condensation" of dissolved Bi with formation nanoclusters Bi embedded in a crystalline lattice  $C_{60}$ . The absence on diffraction patterns of Bi reflexes even at  $C_{Bi} \geq 50$  at.% testifies for the benefit of amorphous state of nanoclusters of Bi inclined to amorphism in thin films. At  $T_s > 470-480$  K in polycrystalline films with  $C_{Bi} > 50-70$  at.% is observed crystallization and oriented precipitation Bi from a lattice  $C_{60}$ . The results received in this paper are generalized as a diagram of phase and structural states of  $C_{60}$ -Bi nanosystems in coordinates " $T_s$ - $C_{Bi}$ ".



## COMPACTING AND ELASTIC RELAXATION OF THE FULLERITE POWDER

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Fullerene is the new allotropic form of the carbon. It is closed spherical molecule  $C_n$  ( $n > 4$ ). Condensed crystal form of fullerene is called fullerite. At ambient pressure and temperature molecules of  $C_{60}$  and  $C_{70}$  arise f.c.c. or h.c.c. structure with weak Van-der-vaals forces between molecules. Density of such structure is  $1.65 \text{ g.cm}^{-3}$  and bulk modulus is 18 GPa. With increasing pressure higher 20 GPa at  $1000^\circ\text{C}$  fullerite transformed irreversibly to amorphous carbon or diamond, at the pressure range lower there are structural order-disorder phase transition and polymerisation.

Fullerite shows some peculiarity in process of the usual compacting. It is object of this scientific research.

It was estimated 100% density at the compacting of the fullerite powders achieves at the very low pressure approximately 100 MPa. It is explained by small theoretical shearing strength of the fullerite. Calculation produced in this research indicated value of theoretical shearing strength equals 75 MPa.

We studies structural changes at the loading of the fullerite powder in conditions of the free compressing at the room temperature. Fullerite powder is loaded at the 0,3, 1 and 7 GPa. X-ray diffraction of fullerite powder shows f.c.c. structure with  $a=1.416 \text{ nm}$  with absence (200) and (400) reflexes, which are permitted to conditions X-ray diffraction. The absence this reflexes is connected with rotation disorder. At increases compacting pressure above-named reflexes are appeared and their intensity is raised. This is consequence of the development of orientation order. This type order-transition is observed too at low temperature. The most justified model for description order transition in this system is model of attaching or "freezing" fullerene molecules in f.c.c. structure. After taking off load the remanent distortions of crystal lattice are determined by X-ray analysis. It is showed that lattice of fullerite after loading at 7 G Pa have remanent compressing and micro distotions equal 4,2% and  $\Delta a/a=(5-7) \cdot 10^{-3}$  accordingly. These values are caused by the macrostrains approximately 850 MPa as it was estimated by special calculation.

Disintegration of the fullerite compact to powder results in full taking off the elastic macrostrains and consequently to disappearance of microdistortions and returns of the initial lattice parameter. It confirms the full reversibility of the fullerite deformation and elastic relaxation at compacting.

### THERMOELECTRIC STABILIZATION OF CARBON FIBERS.

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Carbon woven materials find extensive application in electrical engineering. They are indispensable for low temperature heating, when it is necessary to have a uniform warm distribution. Stability of electric parameters as well as possibility to use the fabric with needed electric resistance is very important for these materials. It is often necessary to reduce specific electric resistance.

Effect of thermal attack through electric heating on electric resistance of carbon fabric was investigated. Heating process was carried out in the air. The maximum of specimen temperature was 1500 °C. The exposure time at the maximum temperature was 1-3 s, the overall treatment time was 5-25 s depending on the initial material resistance. The proposed method allowed to reduce specific electric resistance of carbon fabrics 2-8 times.

Dynamic of resistance changing as well as dependence of final fabric resistance on used electric voltage and treatment time were studied. It was established that electric resistance drops continuously and very rapidly after crossing the threshold voltage.

Observed great fall of resistance can be attributed to variations in the bulk structure as well as surface processes.

## The Structure and Mechanical Characteristics of Exfoliated Graphite

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It is experimentally shown the influence of conditions of exfoliated graphite (EG) disperse form production on their structural condition and also on electrical-physical and physical-mechanical characteristics of materials producing from them.

By the methods of electronic microscopy and microdiffraction, X-ray-phase analysis, electric conduction and thermo-emf, the change of structural conditions of residual compounds of graphite bisulphite (RCGB) is investigated in the process of production of exfoliated graphite disperse forms and in dependence on degree of oxidation of natural graphite, treatment temperature, pressure and method of expansion (free expansion or expansion in closed volume).

Influence of pressure on temperature of structural conversions of RCGB, that registered on electronic properties jump, is investigated at free expansion. The increase of pressure results in displacement of structural transition in the area of higher temperatures. The dependence of temperature of transition, registered on jump of conduction, on pressure in coordinates  $\ln P$  from  $1/T$  has the liner character, and the value  $\Delta H$ , determined from inclination of this dependence, makes  $70 \pm 2$  KJ/mole. At expansion in limited volume the jump of electronic properties is not observed, and the availability of hysteresis of electronic properties during the process of heating and cooling testifies the structural and phase conversions of the micro areas of RCGB.

It is established that RCGB in all the investigated interval of temperatures ( $200 \div 1000^\circ\text{C}$ ), including high-temperature fast heating, and pressures ( $5 \div 20$  MPa), structurally represent the heterogeneous system, including crystal areas of graphite, areas of structural heterogeneity stipulated by distribution of the rest of intercalate with a various degree of order, and also, at least, two phases of the rest of intercalate of various dispersion.

The temperature of heating, the pressure and the way of expansion determine the qualitative structure and quantitative ratio between phase formations of various character, as well as degree of their disorder i.e. structural condition of the disperse forms of exfoliated graphite.

The influence of the pointed distinction of a structural condition on mechanical properties of materials was studied by the method of repeated-static compression.

It is shown, that by change of structural condition of the disperse forms of exfoliated graphite it is possible to obtain materials with given mechanical characteristics.

STRUCTURE OF FILM COMPOSITIONS  $C_{60}$ -Bi

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Film compositions  $C_{60}$ -Bi were obtained over a wide concentration range by combined evaporation of fullerene  $C_{60}$  and bismuth from Knudsen's cells and by successive evaporation as well. The film compositions were examined by high-resolution electron microscopy and X-ray diffractometry methods. At substrate temperatures 400 - 500 K and deposition rates 0.3-0.5 nm/sec the epitaxial films with close-packed hexagonal structure are depositing on the mica. The orientation of films is (001)  $C_{60}$  || (001) of mica. Bismuth being deposited simultaneously together with  $C_{60}$  finally appears to be distributed nonuniformly across the whole volume of the film. At low concentrations bismuth is noted in the form of deposits 3-10 nm in size distributed across the volume of the film. Selected - area diffraction (SED) of such films doesn't show the metallic bismuth reflexes. Increasing of bismuth concentration in a film up to values < 50% atomic leads to the growth of density and sizes of the deposits and further to the disruption of epitaxy, but the SED still don't show diffraction reflexes of metallic bismuth. We consider this phenomenon as location of bismuth atoms in octahedron holes of fullerite lattice and accumulation of these atoms in adjacent holes, which causes the appearance of sorption contrast. But such clusters don't disrupt the fullerite lattices and this could be seen from the direct resolution of fullerite lattice fringes of the (010) and (110) planes crossing the clusters. When fullerene and then bismuth are applied on mica separately, layer by layer, the resulted deposited films are identical to the films obtained in the course of combined condensation. This is possible only when the atoms of bismuth from the vapor flow, which are adsorbed on the surface of fullerite, have time to diffuse deep into fullerite before the critical nucleus is formed. Under other conditions of deposition ( higher concentration rates and low substrate temperatures ) two-layer films are to grow, i.e. critical kinetic parameters of structure formation are to exist. The electric conductivity of the composition films  $C_{60}$ -Bi is significantly higher than that of pure  $C_{60}$  films.

# THE STRUCTURE and MAGNETIC PROPERTIES of THERMOEXFOLIATED GRAPHITE MODIFIED WITH FERRITE and NICKEL

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The samples of thermoexfoliated graphite (TEG) modified with ferrite and nickel were studied for the concentrations from 10 to 50 mass%. The cylindrical samples with the diameter of 2 mm and the length of 10 mm were compacted under the pressure of  $P < 5.5 \cdot 10 \text{ kg/cm}^2$ . The analysis of the structure has shown that TEG particles have non-equiaxial shape. The edges of the particles obtained under great superheating ( $T > 1100^\circ\text{C}$ ) are loosened and on the surface there are individual impregnations of  $\alpha\text{Fe}$ ,  $\text{Fe}_3\text{O}_4$  and nickel. The photographs of the particles in iron (nickel) radiation show that in general the background on which they are found is rather uniform and this testifies to the uniform distribution of metallic particles over the graphite surface. The pores are arranged in straight and concentric circular chains. In general the particles have a flaky structure while the structure of the compacted samples is microlayered and may influence the anisotropy of properties. The average size of the grains is 3  $\mu\text{m}$ . The total ( $P_T$ ) and closed porosity ( $P_C$ ) are (22-25)% and (16-19)% respectively and they do not change essentially when the pressure of compacting is increased from 500 to 5000  $\text{kg/cm}^2$  which corresponds to the pressure of the maximal density of the samples. At the same time the open porosity decreases with the change in  $P$  mentioned above from 8.6 % to 2.9 % and this fact should be kept in mind when manufacturing packing seals and filters

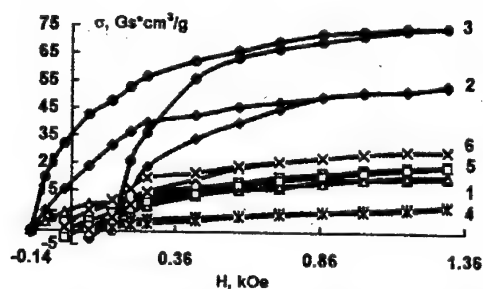


Fig.1. The dependencies of specific magnetization  $\sigma$  vs. magnetic field  $H$  for TEG samples containing  $\text{Fe}_3\text{O}_4$  (1-3) and Ni (4-6) modifiers: 10(1,4), 30(2,5) and 50 % by weight (3,6).

from TEG. The maximal value of specific magnetization ( $\sigma_{\text{max}}$ ) conformably increases as the concentration of ferrite (nickel) in the samples increases. It was found that there exist limiting  $P$  and  $c$  which determine the maximal accessible  $\sigma_{\text{max}}$  for the given type of ferromagnetic component.

### **Low-Density Graphite-Carbon Composite Materials and Their Mechanical Properties**

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One of the present-day directions for the composite materials creation is the elaboration of new carbon materials (CM) on the basis of exfoliated graphite (EG). Chemical modification of the EG particles surface with the thermoreactive organic compounds allows to form quasiuniformly distributed carbon structures in graphite matrix and due to this qualitatively exchange physical and mechanical characteristics of obtained CM. It gives the possibility to use them as mechanical seals, electrotechnical, antifriction and construction materials.

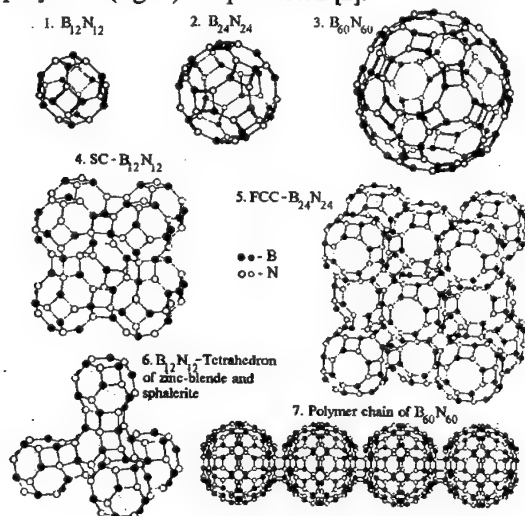
Investigations of the mechanical characteristics at single-axial compression in repeated-static loading regime of porous specimens from EG, CM EG-carbon and CM EG-carbon-carbon fiber with density  $1.0 \text{ g/cm}^3$  have been provided. Compositions of EG-carbon were prepared by modification of EG particles surface with thermoreactive polymer and following compacting and carbonization of the specimens. As a result of this process two mutually penetrated structures from crystalline graphite and amorphous carbon material were formed in CM.

Comparative analysis of the compression diagrams and calculation of the elastic coefficient showed that the behavior of compacted EG has elastic-plastic character under compression. Introduction of carbon into EG up to concentration 35% vol. changes the character of material behavior under compression and increases the absolute magnitudes of the compression characteristics at large deformations. The elastic coefficient of EG specimens continuously decreases with the deformation increasing, but elastic characteristics of CM EG-carbon material are stable to destruction. The introduction of 0.5÷1.0% vol. carbon fiber into EG-carbon compositions leads to 3÷5 times compressive stress increasing at the same deformations. These specimens acquire the elastic material properties and the failure has brittle character when carbon concentration in material increases.

# BN-fullerenes and BN-fullerites - fulborenes and fulborenites

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Discovery of fullerenes has given impetus for search and synthesis of new class of materials - fullerites, endohedral  $M@C_n$  and exohedral complexes (fullerides), multiwalled nanotubes, nanoparticles, etc., their inorganic analogues on the base of  $B_xC_yN_z$ , BN, etc., BN-auxetic material and diamond-like boron hydride [1]. We propose here the molecules  $B_{12}N_{12}$ ,  $B_{24}N_{24}$  and  $B_{60}N_{60}$  (named us as fulborenes, figs. 1-3) in the capacity of boron nitride analogues of the fullerenes. Ten possible crystals built from the molecules (named us as fulborenites, figs. 4-6) and BN-polymers (fig. 7) are predicted [2].



Comparison of their lattice parameters and densities with explosive experiments allow us to identify the simple cubic fulborenite  $B_{12}N_{12}$  with intermediate phase of BN (fig. 4). Density of bcc-fulborenite  $B_{12}N_{12}$  must be 1.5 smaller than sphalerite ("super-dense diamond"). Like zeolite, fulborenites contains porous channels, that in couple with their skeleton high strength make them possible to

use in the capacity of molecular sieves and nanomembranes, as well as intercalated fulborenides as nano-composites.

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MODELLING OF FULLERENES NANOSTRUCTURES WITH  
MOLECULAR DYNAMICS METHOD

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The molecular dynamics computer program is developed, that is based on the semiempirical quantum chemistry MNDO method [1,2]. This program was used for calculating the parameters of spherical fullerenes  $B_{12}N_{12}$ ,  $B_{24}B_{24}$ ,  $C_{24}$ ,  $C_{48}$  and deformed fulleren  $B_{24}N_{24}$ . By relaxation of initial configurations of this fullerenes the equilibrium configurations are obtained.

For the equilibrium configurations the bond lengths and angles, the heats of formation and electronic energy spectra are obtained. The deformed fulleren  $B_{24}N_{24}$  during relaxation has converted into the two planes, interacting by van-der-Vaals forces.

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### STRUCTURE AND LATTICE PARAMETER OF THIN FULLERITE FILMS C<sub>60</sub>

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Thin films of fullerite C<sub>60</sub>, obtained by the method of evaporation and condensation of molecules C<sub>60</sub> on single crystalline and amorphous substrates, were investigated in the temperature range 80 – 300 K by the electron-optical methods of high resolution (direct lattice resolution, selected area diffraction). The structure of the films was varied from a epitaxial with (111) orientation to a highly disordered nanodisperse with the grain 3-4 nm one or amorphous under variance of the condensation temperature.

The films condensed on (100) surface NaCl at the room temperature had an FCC lattice. The crystallographic conditions of the conjugation of (100) surface NaCl and epitaxial fullerite films and the multi positional character of their structure were established.

The films condensed on cooled glass surface had amorphous-crystalline structure. The amount of amorphous phase was reaching 70%. Diffraction patterns of amorphous fullerite were obtained. Values of  $K = 4\pi \frac{\sin \theta}{\lambda}$  for first three halos were determined. The halos positions point out that structure of amorphous fullerite can be described by hard spheres liquid model.

The linear coefficient of thermal expansion was determined from the temperature dependence in temperature range 80-260 K. The increase of the linear coefficient of thermal expansion inversely with the film thickness (3-10 nm) is the size effect due to an influence of the surface.

The phase transition FCC – SC and the step value of films lattice parameter are close to that for a bulk fullerite.

In accordance with obtained results the structure formation mechanism of condensed fullerite films C<sub>60</sub> was proposed.

## GRAPHITE MATERIALS FOR LITHIUM-ION POWER SOURCES

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Industrial and natural Ukrainian graphites and raw materials modified on their basis for anodes of lithium accumulators have been investigated.

The main regularities connecting graphite structure and its electrochemical activity in the process of lithium intercalation in non-aqueous electrolytes have been determined by the methods of potentiodynamic and galvanostatic cycling as well as by the methods of X-ray diffraction analysis.

The method of graphite modification allowing to increase specific characteristics of anodes has been chosen.

The modification method allows to produce powders, having worm-like shape which can be pressed and rolled without a binder. In this case slight change of lattice parameters and crystallite size are observed.

Specific capacity of modified graphites in contrast to the initial ones depends insignificantly on the type of the graphite used.

Electrolyte composition is one of the factors, determining the formation of graphite surface layers. These layers affect the possibility of graphite functioning as anode material. The influence of electrolytes based on the mixture of such solvents as ethylene carbonate and dimethyl carbonate with conducting additives  $\text{LiPF}_6$  and  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ , propylene carbonate, dimethoxyethane  $\text{LiClO}_4$ , propylene carbonate, diglym  $\text{LiBF}_4$  has been studied.

The tests were carried out over the potential range of 40-500 mV/cm<sup>2</sup> with lithium electrode in the cans of 2325 cells.

The influence of the cathode based on the lithium spinel of manganese dioxide on graphite materials capacity in the actual samples of lithium power sources is investigated.

RESEARCH OF THE FAST THERMOGRADIENT METHODS OF  
DERIVING OF CARBON MATERIALS AND ITEMS OF THE  
FUNCTIONAL APPLICATION

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Thermogradient gasphase technologies of carbon and carbon - carbon materials deriving for many years were used mainly for deriving items of rocket engineering and brake disks for airplanes [1-4]. Now in Ukraine and other countries there is an actual problem of conversion of the previously created capacities for manufacturing of economic products. The problem can be solved by the reduction of the production cost and development of new fast methods of the gasphase impregnation of the porous fillers[2, 5-6].

In the present report the theoretical model of the thermogradient gasphase methods, outcomes of experimental researches on their boosting including a forced filtration of the hydrocarbon gas through an impregnating medium is represented. The main performances of the received materials and items on the basis of carbon filaments, powders of electrode graphites, natural graphites a Zavalje deposit, thermo-expanded graphites are represented.

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RESEARCH a GASPHASES CATALYTIC DEPOSITION  
PYROCARBON ON CATALYSTS of an IRON SUBGROUP.

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The catalyst of hydrocarbon on metals of an iron subgroup represents a large scientific and practical interest both for suppression of these reactions in installations of petroleum and hydrocarbon processing and for production of carbon deposits as nanometric powders, tubes, filaments, which are used in production of sorbents, molecular sieves, plastic, rubber technical items and etc. [1-3].

In the present report the outcomes of researches on reaction of carbon deposits catalytic formation in a stream of the raw natural gas, at 400-950° C. are represented As the catalysts the powders of metals and their watersoluble salts both pure and on the carriers from the powders of electrode graphites, termo expanded graphite, paper coke and etc. were used. The new methods of catalytic carbon formations deriving with the use of a hydrocarbon gas forced filtration through the reactor with the catalyst, drop input of the catalyst and continuous removing of carbon formations are discussed. The outcomes of X-ray -structural and electronic microscopic researches of catalytic formations are shown and discussed.

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### INFLUENCE OF SILICON ALLOYING ON UKPM PROPERTIES

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The present work examines the physical properties of the UKPM (carbon carbon composite material with layer-by-layer reinforcement) alloyed with silicon. Silicon was introduced into the material in several ways: 1) by adding into the binder, 2) by applying the already prepared prepreg onto the surface, 3) by impregnating the UKPM with silicon after thermal treatment and densification with pyrolytic carbon. The amount of the introduced silicon varied from 1 up to 15 weight percents.

The dependence of the coefficient of linear thermal expansion on the silicon content has been determined. It allows to draw a conclusion that the introduction of silicon does not cause considerable changes in this parameter.

With the increase in the silicon content there is some increase in oxidizing resistance. This phenomenon can be connected with modification of the microstructure of the binder coke and the composite material itself (a large amount of the introduced pyrolytic carbon).

It has been determined, that within the whole range of the silicon content the bending strength, the compression strength and the laminar shear increase with the increase in density of the material as well as with the increase in the silicon content. With identical density of the material the indicated properties obtain equal values for different values of the silicon content.

The tensile strength much less depends on the density of the material and is determined to a greater degree by the filler properties. For samples with identical density the tensile strength increases practically twice as much after transition from TTH-2MB filler to "Ural" T-22.

Thus, it is possible to draw the following conclusion: the change in physical properties of the UKPM material caused by silicon alloying does not lead to the narrowing of the field of its possible application.

**SEMINAR I.  
HIGH PRESSURE COMPOSITES**

**260-272**

### NANOPARTICLES OF DIAMOND

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The manuscript is devoted to production of diamond nanoparticles (DN), to research of their some properties. It is shown, that DN are formatted by simultaneous condensation of the vapor C and the vapor of vacuum oil  $C_6H_4(COOC_8H_{17})_2$  on one base. For separation of DN and of graphite particles the base placed in big gradient magnetic field. It is proved, that nanoparticles evaporate from a source (a suspension, heap of a powder) as whole (as Brownian particles). The intensity of evaporation depends on the particle size  $d$ , adhesion forces, temperature and gradient of an electrical field, DN are moving in a volume of the source. This motion is by cause of sintering without of compacting.

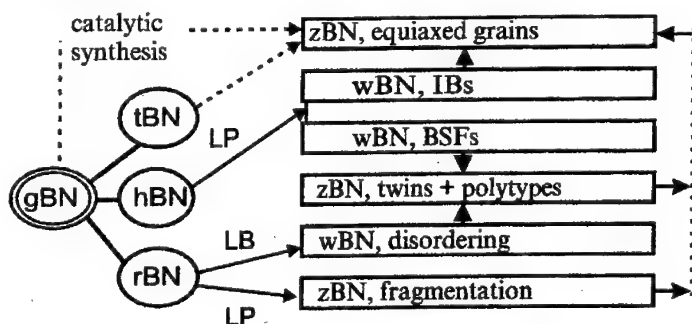
It has been established, that Laplace pressure in DN is about 20 GPa. This pressure is comparable with of pressure interval of diamond synthesis (4—10 GPa and  $T = 1273—1873$  K). This is why DN are stable. It has been establish that DN back temperature is decrease when  $d$  is decrease.

# SYNTHESIS OF HIGH PRESSURE PHASES OF BN WITH CONTROLLED REAL STRUCTURE

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Under high pressures graphite-like modifications of BN (gBN) with hexagonal (hBN), rhombohedral (rBN) or turbostratic (tBN) structures transform into dense diamond-like modifications (dBN): wurtzitic (wBN) or zinc-blende (zBN). The formation of wBN or zBN phase is determined by the mechanism of transition, which in turn depends on initial gBN structure and p,T conditions. The ways of transformations development are shown in the scheme:



The stable high pressure phase zBN is formed as a result of diffusion transformations. The wBN is the metastable phase and it forms only by martensitic transition of gBN. The hBN → wBN transition is developed by layer puckering mechanism, and rBN → wBN transition - by layer buckling one. During the hBN → wBN transition the inversion boundaries (IB) are generated, their formation is bound up with puckering mechanism. The formation of wBN from rBN is connected with basal stacking faults (BSF) generation. Both types of defects play an important but opposite role in the processes of wBN → zBN transitions. IBs impede the stacking sequences rebuilding, while BSFs initiate such transition because these are the nuclei of cubic phase in wurtzitic BN.



### PROMISING CBN MATERIALS FOR PRECISION AND HIGHLY PRECISION CUTTING

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Precision and highly precision cutting as a method of finish machining hardened steels, cast irons and refractory alloys has indisputable advantages over grinding and polishing in view of the generation of precision nominal profile of a high-quality workpiece surface. Widening technological potentialities of superhard materials based on diamond-like phases of boron nitride, specifically for precision machining, requires both essential changes of their physico-mechanical properties and perfection of structure. This was shown by the example of ultradispersed hexanit-P [1], whose structure features allow the required geometrical parameters of the tool cutting elements to be obtained (the cutting edge radius  $r = 0.04-0.06 \mu\text{m}$  with roughness of the edge-forming surfaces  $R_z \approx 0.025 \mu\text{m}$ ).

It has been found that such ultradispersed structures of polycrystalline cBN of Knoop hardness  $\geq 50 \text{ GPa}$  develop during direct phase transformations which proceed in bulky CVD materials based on graphite-like phases of BN - hexagonal (hBN) and rhombohedral (rBN). The principles are formulated of preparing high-strength isotropic and textured cBN materials with a high level of intergranular cohesion and abrasive wear resistance. Both diffusion transformations and crystal-oriented transformations according to  $\text{hBN} \rightarrow \text{wBN} \rightarrow \text{cBN}$  and  $\text{rBN} \rightarrow \text{hBN} \rightarrow \text{wBN} \rightarrow \text{cBN}$  schemes form the basis for the methods. It is expected that the effect of wear-resistance anisotropy which are due to crystallographic texture of the polycrystalline cBN material can be efficiently used in tools which allow for the spatial orientation of a cutting insert with respect to a workpiece.

1. P.V. Zakharenko, V.M. Volkogon, A.V. Bochko, et al., Technological peculiarities of machining using tools of polycrystalline superhard materials [in Russian], Naukova Dumka, Kiev, 1991, 288 p.

**COHERENT PHASE TRANSFORMATIONS AS A BASIS FOR  
PRODUCTION OF HIGHLY TEXTURED POLYCRYSTALS OF  
BORON NITRIDE DIAMOND-LIKE PHASES.**

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The highly textured BN polycrystals with wurtzitic (wBN) or zincblende (zBN) structures can be prepared from textured graphite-like phases by means of coherent martensitic transformations under high pressures. This work deal with features of such transformations and with structure of highly textured diamond-like polycrystals.

The graphite-like modifications with hexagonal (hBN) or rhombohedral (rBN) structures obtained by CVD method were used as starting samples. The initial CVD BN has the form of plate with grain sizes up to hundreds  $\mu\text{m}$ . The [0001] axis of all grains were oriented normal to the growth surface. The p,T treatment of CVD gBN was made in toroid-type apparatus at  $p > 6$  GPa and temperatures 1000 - 2200 C. The two chains of transitions were realized: 1) hBN  $\rightarrow$  wBN  $\rightarrow$  zBN and 2) rBN  $\rightarrow$  wBN  $\rightarrow$  zBN. The formation of wBN occur by different martensitic mechanisms for the different initial gBN structures. hBN  $\rightarrow$  wBN transformation developed by layer puckering mechanism that leads to inheritance of texture without grains fragmentation. rBN  $\rightarrow$  wBN transformation take place by means of layer buckling mechanism which accompanied by rebuilding of initial texture. The wBN  $\rightarrow$  zBN transformation in both cases is developed at  $T > 1500$  C by rebuilding of stacking sequences with the help of stacking faults generation. The wBN texture is inherited by zBN phase.

Thus two types of highly textured polycrystals of diamond-like BN phases may be obtained on the base of CVD BN plates by using of coherent martensitic transformations. The highly textured polycrystals can be used for preparation of crystal-oriented instrument with high functional properties.

INTERACTION OF ULTRADISPERSED DIAMOND AND THE NON-DIAMOND FORMS OF CARBON IN CONDITIONS HIGH STATIC PRESSURE.

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The ultradispersed diamond (UD) owing to its surface and catalytic activity, and also the structure making properties is a perspective component for obtaining composite superhard materials of a new generation.

In the present work the methods of X-ray diffraction and electron microscopy investigated influence of the components UD on sintering and phase transformations of the non-diamond forms of carbon in conditions of high static pressure. Non-diamond carbon was in a mixture in a free condition in the form of graphite, or structurally was connected to UD surface.

Established, that in conditions, close to conditions of catalytic synthesis of diamond in presence UD there is a transition of non-diamond carbon into diamond, depending on a consistence and structural condition of non-diamond carbon the process of synthesis realised in different ways.

Is determined, that already at temperature of processing of a mixture below 1000 °C transformation of graphite into diamondlike carbon modification with parameters of a lattice  $a_0 = 2,5 \text{ \AA}$ ,  $c_0 = 16,4 \text{ \AA}$  has been observed. At further growth of temperature were captured hexagonal diamondlike modification with parameters of a lattice  $a_0 = 2,52 \text{ \AA}$  and,  $c_0 = 12,35 \text{ \AA}$  and diamond. Thus the increase of microhardness and density of the sintered samples was detected. The intermediate structures have not been found, when connected to diamond's surface amorphous carbon have been presented in the material. The increase of temperature and time of sintering results in graphitization of a material and decrease of its physical and mechanical characteristics.

Results of the work testify that the UD additions result in change of properties of carbon materials, sintered in conditions of high pressure. Thus capabilities for designing of a microstructure of such composites essentially extend.

### PRODUCTION OF POLYCRYSTALS cBN BY A DIAMETER 30-40 mm AND AREAS OF THEIR APPLICATION

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The concept of creation of polycrystalline superhard materials on the basis of cubic boron nitride (plate of 30-40 mm) with high physico-mechanical properties is based on the following approaches:

- Reception of structure with a continuous skeleton cubic boron nitride and binding phase, distributed on borders, from refractory connections ensuring high hardness and transcrySTALLITE character of destruction;
- Management of processes of formation of solid solutions on the basis of a crystal lattice cubic boron nitride, allowing to change hardness of materials;
- Creation of optimum concentration of defects in structure of cubic boron nitride, ensuring a necessary parity of hardness and fracture toughness of polycrystals

These approaches are realized at creation of a polycrystalline superhard material Kiborit (trademark uniting the wide nomenclature of tool and constructional materials of the system cBN-AlN).

The way of reception of polycrystals cBN by a diameter of 30-40 mm (kyborit-2) provides an output on technology, which save up energy and materials, in which basis - use steel HPA and significant decrease p, T-parameters of sintering.

In the nomenclature of leading firms of the world there are no polycrystals cBN by thickness more than 8 mm. Polycrystals cBN by a diameter of 30 mm, thickness 25 mm with a high level of physico-mechanical properties (kyborit-2) are used as constructional materials, for example, for manufacturing components of multiple anvils.

The reception in one cycle of sintering of polycrystals KHB of large volume provides also economic feasibility of creation of powders cBN of a wide spectrum grain size with polycrystalline structure and with high abrasive ability.

# STRUCTURE MECHANISMS OF PLASTIC FRAGMENTATION IN NON-METALLIC CRYSTALS UNDER THERMOBARIC TREATMENT

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In the paper structure formation mechanisms for disoriented (fragmentated) deformation substructures and their evolution with temperature (1200-2000 °C) at high pressure (7,7 GPa) are considered for three crystals types (with diamond lattice and diamond-like lattices of wurtzite (H) and sphalerite (C) types). The crystals differ by mechanisms of shear deformation. Consideration was carried out on the base of electron microscopy study on polycrystal samples obtained under P-T-treatment of powders.

The first type includes 2H BN, 6H SiC (plastic shifts are realized with participation of splitted basal dislocations). At 1200-1500 °C in the crystals fragmentation of initial particles is due to kinking and formation of reorientation bands (rotation substructures). High angle kink boundaries and disoriented substructures with plane bends (DSPB) are formed. At  $T > 1500$  °C dislocation ordering and formation of dislocation boundaries take place.

Diamond, 3C BN, 3C SiC are concerned to the second type. At the first stage (1200-1500 °C) the crystals are fragmentated via deformational twinning and DSPB formation. Later appear in the regions of nonuniform pile-ups of perfect dislocations. At  $T > 1600$  °C disorientation bands are formed in the crystals having twins and DSPB and as a result further fragmentation takes place. Also local rearrangements of thin deformation twins into dislocation boundaries occur in diamond and 3C BN.

The third type is presented by AlN. Only perfect dislocations take part in the deformation of AlN crystals. At  $T = 1200$  °C high density of extinction bending contours composed by dislocation pile-ups is formed and caused appearance of DSPB. At  $T > 1400$  °C dislocation pile-ups transform into various dislocation boundaries.

## ON THE FORMATION OF A COMPOSITE STRUCTURE DURING cBN SINTERING WITH ALUMINUM

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Studied was the formation of a composite structure during sintering a mixture of cBN and Al powders under high pressures (2.5 to 8 GPa) and temperatures (up to 2100 K). The effects of p,T -parameters on the following physicochemical processes were investigated: - generation of open and closed porosity during sintering cBN powders; - wetting and infiltration of cBN with aluminum; - yielding of products of interaction between cBN and aluminum melt ( $\text{AlN-AlB}_2\text{-AlB}_{12}$ ).

X-ray diffraction was used to examine the phase composition of the composite material, while the distribution of phases throughout the bulk of the material and the mode of crack propagation during the material fracture were studied by electron microscopy and fractography. We have also studied hardness of the composite as a function of infiltration and sintering parameters.

In the 2.5 - 8 GPa range, the pressure dependence of the onset temperature of cBN wetting with Al is given by the equation:  $dT/dp = 68$  K/GPa, and the pressure dependence of the onset temperature of the chemical interaction between cBN and aluminum melt is  $dT/dp = 15$  K/GPa. This reaction results in crystallization of aluminum refractory compounds (aluminum nitride and one or two aluminum borides) from the melt. Phase compositions of the reaction products that form a binder of the composite as well as phase distribution over the composite structure are defined by p,T-conditions of the infiltration and sintering.

A structure characterized by the continuous skeleton of cBN and a binder that is uniformly distributed along cBN grain boundaries ensures optimal properties of the composite. This composite exhibits transcrystallite fracture. The binder along the grain boundaries hinders propagation of cracks.

# EVOLUTION OF THE REAL CRYSTAL STRUCTURE OF CUBIC BORON NITRIDE DURING HP-HT SINTERING.

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The evolution of the real crystal structure of cubic boron nitride during HP-HT sintering of polycrystals has been studied depending on grit sizes and synthesis conditions of the initial powders. The sintering was performed in a toroid-type high pressure apparatus using a graphite heater in the 300 to 2700 K temperature and 2.5-7.7 pressure ranges.

X-ray diffraction was used to study the powders before and after p,T-treatment. Characteristics of the real crystal structure (lattice constant, Bragg scattering area and microdistortion value) of cBN samples were determined to a high precision using an automated system for collection and computer-aided processing of X-ray diffraction spectra. By processing a great number of experimental data with methods of mathematical statistics, the effect has been established of conditions of synthesis of the initial cBN powders and sintering temperature on the lattice constant and the peculiarities of formation of dislocation structure of polycrystals.

The cBN lattice constant-synthesis conditions relation inherent in the initial powders retains after HP-HT sintering.

The increase in the lattice constant of polycrystals sintered at 1600, 1750, and 2100 K correlates with generation of defects of the crystal structure.

**STUDY OF STRUCTURE-FORMING OF POWDER GRANULES ON  
A HEXAGONAL BORON NITRIDE BASE AT IMPULSE ACTION  
ON FINELY DISPERSED POWDERS  
AND COMPOSITIONS**

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A complex of researches of powders of boron nitride of low-temperature and high-temperature synthesis in a starting state and after processing by explosion has carry out by authors. A combination of high-pressure and temperature, the major degree of a plastic deformation of a loaded body promotes formation strong inter-particle contacts such as welding having high endurance. The phase composition of powders was determined with methods of the quality and semiquantitative X-ray diffraction analyses. The powder of high-temperature synthesis has the most perfect crystalline structure — physical line broadening in it minimally. The linewidth (212), (216) at a powder of high-temperature synthesis in a starting state practically does not differ. After action of explosion there is a considerable distinction, that can be echo effect of the growth of microstresses created by a deformation of a crystalline grating at explosion, and also with increase of ultradispersivity of a block structure. Characteristically, that the linewidth (212), (216) at a powder of low-temperature synthesis in a starting state differs. After action of explosion this distinction is saved. For low-temperature modification of boron nitride the fracture of a compact set obtained by an explosive pressing up to a state of a powder material is characteristic. The fracture flows especially effectively under action of a light. After fracture the linewidth are decreased, that can be echo effect of relaxation of microstresses created by a deformation of a grating at explosion, and also with increase of the size of blocks of ultradispersivity of a block structure. It is possible to assume, that the distinction in a state of high-temperature and low-temperature modification of a powder of boron nitride is determined with a different degree of diminution of crystalline structure of these powders, and in particular turbostratifying. The attempt of an estimation of turbostratifying of powders have been make. In results it differs on the order. The high-temperature modification of a powder BN can be refereed to turbostratifying on obtained value of coefficient of turbostratifying and other attributes of a lines profile, that essentially has an effect for the content in a starting powder BN (98-98,5%) and its properties and behavior at high pressures and deformations.



**THE INFLUENCE OF THE CONTENT OF  $B_2O_3$  IN  $BN-B_2O_3$   
COMPOSITION ON THE PHASE TRANSFORMATION  
PARAMETERS AT HIGH PRESSURE**

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P,T parameters of phase h→c transformations in boron nitride are strongly dependent on the degree of crystal perfection of the structure and on the dispersity of the starting graphite-like boron nitride. Various points of view concerning this dependence, sometimes conflicting, exist in scientific literature. The authors carried out a detailed study of phase transformations in ultradispersed boron nitride obtained by the method of plasmochemical synthesis.

It is possible to obtain ultradispersed BN powders with specific surface from 700 to 100 m<sup>2</sup>/g, depending on the synthesis parameters, which corresponds to an average particle size from 4 to 15 nm. Phase transformations in ultradispersed BN were examined in the pressure range 5.5-7.7 GPa and in the temperature range 1070-1670 K.

A dependence of the degree of h→c transformation in boron nitride on the sizes of starting phase particles and the degree of oxidation was studied. It is shown that pre-oxidation of the starting powder considerably increases the degree of the phase transformation.

It was found out that a direct phase transformation to cubic modification occurred in ultradispersed BN at anomalously low P,T parameters. An explanation of the obtained results was given on the base of the precise study of the boron nitride structure.

# APPLICATION OF NANOPOWDERS FOR STRENGTHENING OF COMPOSITE BASED ON DIAMOND AND SILICON CARBIDE

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Density, strength and structure of composite obtained under silicon impregnation into diamond micropowder compact at high pressure and high temperature have been studied. It was determined that if diamond and silicon carbide nanopowders were introduced in the system, the yield of samples without external defects increases. Average value of compression strength for such composite is 2,2 GPa and for material produced by usual technology is 1,7 GPa. Density of the obtained material runs  $3,43 \pm 0,02$  g/cm<sup>3</sup>.

Comparative study on the materials structure by the method of transmission electron microscopy shows that strength increase is caused by the following factors: high dispersity of the silicon carbide grains (<1  $\mu$ m) formed at the interaction of silicon with diamond particles; inconsiderable quantity of inclusions of free silicon (<5 mas.%); uniform distribution of binding SiC phase between diamond grains and high strength of conjugation boundaries diamond-SiC.

## THE INTERACTION OF THE ULTRADISPERSIVE DIAMOND WITH THE BN AT HIGH PRESSURES AND TEMPERATURES

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Like a diamond cubic boron nitride has the high hardness and semiconductor properties. Because of the great importance of the cubic BN (c-BN) phase, there are many works about the P,T - conditions of the transformations from hexagonal BN (h-BN) into c-BN with the presence of the different compound-catalysts. A new direction in the investigation of nanomaterials began to develop at the last time. Nanomaterials have many unique physical and chemical properties. Because of that, the great practical interest is to receive and to investigate the materials, which combine unique properties of the nanophase materials (UDD specifically) and c-BN. The experiments were carried out on the three groups of the samples with the concentrations of 10:90, 20:80 and 50:50 wt % of the h-BN and UDD respectively at the pressure 7.0 GPa and the temperature range 1000-17000C. The time of the thermal treatment were 5-60 s.

The thermal treatment under high pressure was based on the high pressure apparatus of the toroidal type. The X-ray structure analysis were performed on the X-ray diffractometer URS-50IM. The microhardness of the samples were measured on the apparatus PMT-3. The density of the samples was measured by the method of the hydrostatical weighing in CCl<sub>4</sub>.

The character of the changes of the density (and microhardness) of the samples, their phase compositions and the microstructures on the time and temperature of the thermobaric treatment indicate the presence of two competitive processes: 1 - the direct aRb transformation in BN and the sintering of materials; 2 - the inverse bRa transformation and the graphitization of UDD particles.

The processes of interaction one can imagine as follows:

1.  $t < 30$  s. Partial synthesis of c-BN. The density and microhardness are small.
2.  $t = 30$  s. The sintering of the c-BN and UDD material, with partial recrystallization of the UDD. The density and microhardness are the maximum.
3.  $t > 30$  s. The graphitization of the UDD particles and the inverse c-BN → h-BN transition. The density and microhardness decrease.
4.  $t = 30$  s.  $T = 14000$  C. The synthesis of the diamond from the graphite and the synthesis of the cubic BN from the hexagonal BN, with simultaneous sintering of the material. The density and microhardness increase.

**SEMINAR J.**  
**POWDER METALLURGY**

**274-309**

MANUFACTURING OF THIN, HOLLOW METALLIC FIBERS BY  
THERMAL DECOMPOSITION OF ORGANOMETALLIC  
COMPOUNDS USED TO  
PRODUCE HIGH PERFORMANCE FILTERING AND  
CATALYTIC STRUCTURES

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The available methods of preparing metal fibers by drawing through a die provide fibers with a minimum diameter of 0.020 to 0.030 mm. It is frequently the case when fiber diameters of 0.010 to 0.005 mm are required. For instance, to produce fine filters, electrodes for chemical power sources, in catalyst chemistry, etc.

The authors have developed a method for manufacturing of hollow fibers of nickel, cobalt or copper having dia. of 0.006 to 0.010 mm using thermal decomposition of corresponding organometallic compounds upon the surfaces of carbon fibers of various semiproducts like braid, knittweaves, felt measuring 0.15 to 15 mm in thickness, and examined some properties of these. Said semiproducts were infiltrated with an appropriate organometallic compound with subsequent drying and thermal treatment under reducing or neutral medium which resulted in pyrolytic decomposition of OMC with formation of a metallic (Ni, Co, Cu or Fe, or their combination) coating on the fibers. The process features in that all the fibers through the semiproduct bulk are covered with a film.

During the further operations of thermal treatment, carbon is evacuated and hollow metallic fibers dia. of 0.005 to 0.010 mm were prepared that had a specific developed structure and a high specific surface.

The effect of processing parameters like solvent concentration, pyrolysis temperature and time, fiber mass ratios and OMC concentration effect on the metal yield in a coating, and the coating and fiber structures, was examined.

The hollow fibers as obtained were used to prepare filtering materials and their characteristics like density, porosity, pore sizes and shapes, and gas permeability, were studied.

# RESEARCHES IN THE AREA OF DEVELOPMENT POTENTIAL POWDER MATERIALS FOR BRAKE APPLICATION

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At present, the transport means use braking shoes made of polymer matrices. They are reinforced with asbestos, polymer, metallic or mineral fibers, and comprise various fillers.

Tests of composites (CM) on tribological behaviour have confirmed their efficiency and high wear resistance at the temperature of up to 200 °C in the friction zone. As disadvantage of these materials, a considerable reduction of the braking efficiency and increase of the shoe wearing rate occur in the friction zone at over 200 °C during the long-time braking.

The promising powder material (PM) based on a metal matrix has no asbestos and polymer, and is produced by powder metallurgy techniques using powders of metallic and non-metallic powder mixture with subsequent sintering under specific conditions. Up-to-day materials science approach to the "design" and selection of processing conditions for preparing products, in view of the brake features, provides high tribological characteristics of PM and its advantages over CM.

The PM and CM have the coefficient of friction of 0.38 to 0.39 at its stability of 0.9 at the friction velocity of 5 m/c and the temperature of up to 100 °C of the friction zone, on iron. The PM has wear resistance 2 times as much as CM's.

The tribological characteristics of PM and CM are practically equal at the velocity of 10 m/c and the temperature of 100 °C in the friction zone. The coefficient of friction for CM on iron reduces to the value of 0.25 with increasing the zone temperature up to 300 to 350 °C, i.e. the braking efficiency decreases for 24 %, while the coefficient of friction of PM remains at the level of 0.33. The specific wear rate of CM is superior to that of PM (over 3 times).

**DEVELOPMENT OF PRODUCTION TECHNOLOGY OF HIGHLY  
ACTIVE IRON POWDER FOR FRICTION,  
ANTI-FRICTION AND ELECTRICAL MATERIALS**

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A technology for producing iron powders of the new class viz so-called «light» iron powders with the apparent density of 1.2-1.8 g/cm<sup>3</sup> and a compact strength of 60-100 MPa has been developed by the Institute for Powder Metallurgy of TsNIChemet and tried-out under production conditions of JSC «Sulinski Metallurgical Works». These powders exhibit high activity during sintering since specific surface area of such powders is over 2.5 m<sup>2</sup>/g, tens times more than that of conventional iron powders of ПЖВ4- or ПЖВ2-type. Testing of «light» iron powders has demonstrated high efficiency of their application for improvement of operating characteristics of existing materials and development of new kinds of friction, anti-friction and electric contact materials. Thus, addition of a highly active iron powder to the starting charge ensures the following advantages:

- increase of wear resistance of a pair of friction materials from 50% to 500% on retention of friction coefficients and friction stability at the same level;
- reduction of content and in some cases total elimination of carcinogenic components such as plumbum and asbestos from composition of tribotechnical-purpose materials;
- improvement of a compact strength by 25-50% as well as adhesion with other materials.

VIAM, NIITAVTOPROM, Balashikhinsky LMZ etc. are the participants of the present work.

## NEW TECHNOLOGIES OF PM COMPONENTS MANUFACTURING WITH INNER SPACES

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An increase of efficiency and expansion of PM application in various fields of industry is impossible without research and development of new high-efficient technological processes of producing high density structural parts of different purpose. A density is one of the main characteristic of the parts produced by powder metallurgy method. A high level of mechanical and special properties is usually provided only at under reaching high and homogeneous density of the material. The investigations showed that an effective decreasing of the porosity required significant mechanical loading of compacted material and was connected with local plastic deformations of particles in pores surroundings.

The objective of the present work is an analysis of the densification process of the powder complex shape body (with inner spaces) in the process of hydrostatic compression of the separate elements.

The densification of powder material under hydrostatic loading is connected with decreasing pores volume, mainly as a result of direct deformation of separate parts (inner shear) and to a lesser degree at the expense of their relative (interparticle) shearing.

The investigations had been fulfilled on the installation for axial pseudohydrostatic compression. To execute this scheme of pressing the elastic shells were used. Availability of such elastic medium permits to compact (densify) freely filled powder by means of an axial component of the force and at the expense of transmission into the powder only radial pressure. The small-dispersed nickel powders ПНК1/П8 GOST 9722-79, iron powder ПДК3М GOST 9849-89, partially-alloyed iron powder ПДКН4/П2М TR 14-1-4393-87 and electrolytic copper powder ПМС-1 (GOST 4960-75) were used for the investigation. The polyurethane used as the elastic material. The density of the preforms was measured by the hydrostatic weighing method at БЛН-200М scales with an accuracy to 1 mg (GOST 25281-82). The density distribution of the cross-section metallographic specimen was measured by the stereometric metallography method with using the metallographic microscope МНМ-8.

The experimental data showed that densification of powder material under complicated pressing scheme was submitted to the common mechanism if the separate area is studied. When an axial stress acts on the high-elastic shell the radial forces appear and then they act simultaneously with the axial ones. In result in this area the all-side compression is watched that in our opinion is connected with the deformation of particles themselves and filling up the pores. In this case in initial stages an intensity of the densification is maximum but in final stage it is significantly decreased, at the expense of the plastic deformation at all-side compression.



# DEVELOPMENT OF Ni-Mo POWDERED DEFORMED ALLOYS

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A number of multicomponent alloys containing significant amount of the refractory components and possessing excellent performance characteristics are hard to be hot or cold deformed. The customary metallurgical routes to prepare multicomponent alloys are expensive and in a number of case don't make it possible to prepare qualitative preforms.

During the resent 10-15 years powder metallurgy is widely used abroad to produce pipes of stainless steel and multicomponent alloys which is advantageous in comparison with the customary routes. Basing on the experience in PM and hot pressing we suggested technology to produce pipes of the hard-deformable alloys.

Ni-30%Mo alloy was used for which customary routes to prepare pipes failed. Poor deformability of the alloy is related with the intermetallic precipitation during thermomechanical processing.

The suggested technique to produce pipes of Ni and Mo powders mechanical mixture enabled to avoid intermetallic precipitation in the material structure. The basic principles is on the one hand to preserve high activity of Ni and Mo powders and on the other hand to add plastic deformation activating effect. The alloy formed was practically completely homogeneous with no inclusions present.

The mechanical tests results showed the as-pressed pipes metal to possess good combination of high strength and plasticity (Table).

Material	UTS, MPa	$\sigma_{0.2}$ , MPa	$\delta$ , %
EP-982 Standard Alloy	784	392	40
Powdered Alloy	1050	660	38

Intercrystalline corrosion resistance tests of the material were carried out in the boiling 21% aqueous solution of the hydrochloric acid during 200 hours. Metallographic studies did not reveal intercrystalline corrosion in the samples.

## STAINLESS STEEL BASED COMPONENTS

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In here one can see the results of studies on the influence of sintered composites based on stainless steel X18H15 with  $\text{Cr}_3\text{C}_2$  and  $\text{MoS}_2$  on their properties.

Sintering of composites based on stainless steel of austenite type, comprising  $\text{Cr}_3\text{C}_2$  and  $\text{MoS}_2$  is accompanied with formation of complex heterophase structures, stipulated by Cr- and C diffusion into matrix whereas Fe and Ni come from matrix into carbides and by formation of chromium sulfides and Mo diffusion into matrix.

Control over sintering processes of such materials, as well as adjustment of their compositions provide for highly wear resistant composites designed for various operating conditions.

It has been defined, that an increase of  $\text{Cr}_3\text{C}_2$  content from 1% to 30% results in doubled improvement of composite's wear resistance along with both simultaneous lowering of bending strength and modification of some other characteristics, in particular: hardness and micro hardness of structural components, parameters of crystal lattice base, shrinkage in sintering and the like. The authors have determined the significant difference in properties of  $\text{Cr}_3\text{C}_2$  containing materials versus the same composites, having molybdenum disulfide additionally. The least ones show higher in 2-3 times wear resistance and significantly better hardness as well as parameters of crystal lattice base, however with slightly lower bending strength. The optimum combination of properties is feasible with 20-25%  $\text{Cr}_3\text{C}_2$  and 3-5%  $\text{MoS}_2$  contents in composite.

The composites developed can be used in various branches of technique for manufacturing of corrosion resistant products and also as operating layer in engineering of laminated materials.

## COMPOSITE MATERIALS FOR HIGH-TEMPERATURE UNITS OF FRICTION

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In the present message the researches outcomes of three types of materials intended for a work at increased temperatures are represented:

1. On iron base - powders composites obtained of grinding scraps of the "P6M5" steel for a work at the temperatures up to 500 °C.
2. Composites on the base of Ni-Mo alloy for a work at the temperatures up to 700 °C.
3. Composites on the base of complex-alloyed nickel alloy "ЭП975" for a work at the temperatures up to 900 °C.

In all above-stated materials as effective solid lubrication  $\text{CaF}_2$  was used.

The materials with use of powders-scraps of "P6M5" steel and on nickel base were produced by pressing and sintering at the temperatures 1100-1200 °C, and composites of "ЭП975" powders were produced by gas-static pressing at 1210 °C.

The physic-mechanical and tribotechnical properties of new materials (tab.1 and tab.2) are investigated.

Table 1

Physic-mechanical  
properties of materials

№	Structure, % mass	$\sigma_b$ , MPa	$a_k$ , J/m <sup>2</sup>	HB, MPa
1.	P6M5+5CaF <sub>2</sub>	410-440	610-650	700-800
2.	Ni+27Mo+10CaF <sub>2</sub>	600-700	800-900	1400-1500
3.	ЭП975+6CaF <sub>2</sub>	550-600	550-600	2500-2600

Table 2

Tribotechnical properties of materials

№	Structure, % mass	Tempe- rature, °C	Coeffi- cient of friction	Intensity of wear process, micron/km	Ultima- te load, MPa
1.	P6M5+5CaF <sub>2</sub>	500	0,11	33	7
2.	Ni+27Mo+10CaF <sub>2</sub>	700	0,15	26	7
3.	ЭП975+6CaF <sub>2</sub>	900	0,26	30	7

The industrial technology of making the blanks of sintered bearings of a sliding in material Ni-Mo-CaF<sub>2</sub> for high-temperature friction units intended for equipment the rotary blades of special hardware on SPB "MashProect" (Nikolaev) was introduced.

Antifriction bearing bushes made of the material Ni-Mo-CaF<sub>2</sub> were introduced on "Nevsky zavod" (St.-Petersburg) for equipment the force turbine of the aggregate "TTH-25".

The full-scale tests the sintered bearings of a sliding in material Fe + 50%P6M5 + 5%CaF<sub>2</sub>, installed in rests' friction units of a roller floor of a refrigerator rolled machine "320" on RMZ (Rustavy), have shown, that they on a wear resistance in 3 times exceed used now bearings of a sliding, are reliable in work and ensure long work of friction units. The recommendations about organisation of serial production of an industrial sintered bearings of a sliding for equipment the friction junctions of rolled machine "320" on RMZ (Rustavy) were given.

The obtained data testify to expediency of application the materials with use of powders-scraps of "P6M5" steel, on base Ni and powder alloy "ЭП975" in high-temperature friction units of machines and mechanisms both a metallurgical and power mechanical engineering.

## INFILTRATED POWDER FRICTIONAL MATERIALS

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Wide application of an infiltration method with metal melts of porous powder billets is caused by the possibility of making practically free of pores constructional and antifrictional products with high physical-mechanical characteristics.

Investigations fulfilled in PMRI showed good prospects of using the said method to produce frictional products on iron base for work in conditions of friction without lubricant.

There are proposed various schemes of making frictional products i.e.:

infiltration of a frictional composition preliminary pressed on a steel base;

infiltration bilayer compositions (without using steel bases).

It is determined that under some lowering a friction coefficient the investigated materials compositions are characterized by a considerably higher wear resistance and maximally allowed specific friction strength.

Materials infiltrated with copper-zinc alloys are characterized by the best frictional characteristics. A frictional coefficient of the EpOIIIC 5-5-5 bronze and ЛI-80 brass materials infiltrated with melts made 0,34-0,37 (as compared with 0,38-0,40 without infiltration) under the wear-out intensity 0,7-2,0  $\mu\text{m}/\text{km}$  (as compared with 2,1-3,2  $\mu\text{m}/\text{km}$  without infiltration). It is determined that frictional materials infiltrated with bronze are characterized by the higher corrosion resistance by one order as compared with the source materials.

Using the said method it is possible to manufacture frictional products without applying high pressures during sintering, as well as to make sufficiently strong products in the form of cylinders, prisms etc. to use them in frictional constructions as insert elements (brake units of railway transport, clutches etc.).

### **BASALT-CONTAINING ASBESTOS-FREE FRICTION MATERIALS**

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The IPMS of NAS of Ukraine has conducted researches to develop asbestos-free composite materials for frictional application in the brakes and gears. As reinforcing element, basalt fibers have been used that have thermal and physical characteristics mostly close to those of asbestos, besides have elevated elastic modulus and chemical resistance.

Binder compositions have been selected and formation conditions adjusted for frictional composite materials. As functional additives, metallic oxides as well as bronze or brass cuttings were used. Wax compositions were selected that ensure a maximum wettability of basalt fibers with a polymer binder.

Prototypes of materials have been prepared subjected to laboratory and bench testings. compositions and process conditions of composite formation have been adjusted in the result of these testings. Experimental lots of brake shoes were fabricated, and these were successfully tested at automobile building plant, Zaporizhya.

The materials developed are intended for the use in a broad range of industries and this will reduce the need in non-available components for vehicles and agricultural technique application.

### **MECHANICAL AND TRIBOTECHNICAL PROPERTIES OF HIGH DENSITY ANTIFRICTION FERROGRAPHITE MATERIALS FOR INTERNAL COMBUSTION ENGINES**

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Dense powder products (relative density above 0,9) received with the help of hot forging, punching, double pressing - sintering, injection forming, high-temperature sintering and warm pressing are widely used for important units in the motor industry, specifically in friction joints.

This work shows the basic capability of obtaining dense powder ferrographite materials with a high content of graphite by double pressing - sintering. Research covered the dependence of mechanical and tribotechnical characteristics of the obtained materials on the graphite content in a blend.

Use of double pressing - sintering technology increases 2-3 times strengthening and 1.5-2 times tribotechnical properties in comparison with similar properties of powder materials of the same structure, which originated from the traditional single pressing and sintering technology. The comparison shows that the deterioration intensity of ferrographite materials is more than 10 times lower than that of bronze. The friction coefficient and average temperature on a friction surface are dropping. Use of material originated from the new technology without expensive alloying additives, for manufacture of valves guides of an internal combustion engine of the motorcycles "Dniepr-16" has 4 times increased service life of the joint. Similar materials can be used for saddles of valves and other units of engines.

Thus, new technology has been developed for manufacturing dense (91-94 %) ferrographite materials with an increased graphite content (2 - 3.5 mass. %) which resulted in combination of high mechanical and antifriction properties with good economic indexes and in application of such materials to internal combustion engines.

Researches of materials obtained by double pressing - sintering, were financed by the Ukrainian Scientific - Technological Center - an organization created on Ukraine with participation of the USA, Canada and Sweden.

## THE SINTERING OF FINE PARTICLE POWDER TUNGSTEN-SCANDIUM OXIDE BLENDS

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The adding of fine particle oxide powders (1, 5 and 10%) effects on the volume shrinkage of tungsten powders. The coarse and fine tungsten powders with  $\text{Sc}_2\text{O}_3$  additions were studied for two powder blend groups: first – the sizes of tungsten particles were 4 mkm and  $\text{Sc}_2\text{O}_3$  – 0,2 mkm; second – the sizes of tungsten particles were 140 nm and  $\text{Sc}_2\text{O}_3$  – 20 nm.. The powder blends were prepared by chemical deposition of  $\text{Sc}_2\text{O}_3$  on the tungsten powder surface. The identical samples were obtained by the sintering at 2000°C the first group samples and by the sintering at 1000°C the second group samples.

The sintering of samples with the coarse W particles is activated during heating stage by the oxide additions as more than their contents higher. But the additions retard the shrinkage during the isothermal stage of sintering. The sintering of the fine W powder blends is retarded by the fine oxide particles in all cases. Simultaneously the additions of fine particles decrease the specific surface of porous samples during early heating and their microstructure become roughness.

The volume shrinkage of W- $\text{Sc}_2\text{O}_3$  is a function of size factor of system ( $\alpha$ ).  $\alpha$  is the ratio of the small and coarse particle sizes. If  $\alpha$  is 0.143 the shrinkage retarding will take place and depends on the oxide content. If  $\alpha$  is 0.05 the influence of oxide additions is negligible. As a result the relative particle arrangement of metal and oxide components are shifting from matrix-statistic to statistic microstructure.

In the frame of the model of composite blends of V.V. Skorokhod the microstructure matrix is higher the volume shrinkage retarding is greater for equal contents of oxide. This situation is confirmed by experiments with the powder blends having the different quality of blending. The blending is worse the microstructure matrix is higher. If the fine powder particles form the agglomerates the retarding of volume shrinkage is smaller in this case.

The coalescence of fine oxide and tungsten grains by surface diffusion is the main process in early sintering stage. Thus the sinterability of fine metal-oxide blends is depend on the size factor and the relative particle arrangement.

### RECOVERED METALLIC POWDERS FOR SOME NEW COMPOSITE MATERIALS

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Some large amounts of wastes in form of slurry are produced during processing of steel by means of grinding. The composite materials for friction systems are a suitable domain to reuse the recovered metal-abrasive powders obtained from these scrape, by nonconventional means.

The aim of this work was to develop a new economical and ecological method for processing of grinding slimes to friction materials with competitive characteristics like commercial ones.

The recovering of metal-abrasive powders was carried out in a vacuum furnace by a thermal treatment. The method consist of gradually lubricant-coolant removing in form of steams by evaporation and condensation in a condenser placed out of furnace and before the vacuum pump.

The new friction materials of the metallic or semimetallic type based on the recovered steel powders are composites consisting of an organic or metallic matrix in which the following ingredients are dispersed: lubricating, friction, filler, reinforcement agent etc.

The raw materials was processed by powder metallurgy techniques: mixture preparation, blending, cold pressing and sintering, respectively curing, under some certain specific loads.

The sintering of the metallic matrix friction materials was carried at 700...1060°C for 0.5...2 hours with an applied pressure of 0,5...3MPa. It was established that the density, hardness, mechanical resistance, coefficient of friction and wear resistance increase according to the increase of pressure, sintering temperature and specific load.

For the semimetallic friction materials, the cure of the binder was realised at 150...230°C. Simultaneously applied heat and pressure cause the resin melting and flowing throughout the piece, forming a continuous matrix in which the ingredients are dispersed.

The abrasive surface of the recovered steel powders and their irregular shapes are favourable to achieve a high and stable coefficient of friction.

The new friction materials are suitable for heavy-duty brake applications.

This new important class of advanced materials present a higher economic efficiency and environmental compatibility.



### Gas-Dispersed Synthesis of the Metal Oxides Nanopowders

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At this work the possibilities of obtaining the metal oxides nanopowders are considered by the combustion methods. The gas-dispersed synthesis (GDS) method is based on combustion of dust clouds of metal particles in a laminar plume (it can be premixed plume - like Bunzen's burner or nonpremixed two-phase plume - like Burke-Shuman's diffusion burner). The obtained powders are well desagregated, have the spherical morphology, narrow gradation, average size of particles - 0.04 - 0.1 microns. To obtain pure oxide powders of Al, Zr, Ti, Fe, Mg etc. by GDS method it is necessary to use not less pure microdisperse metal powders which are frequently obtained from the appropriate oxides. However, unique properties of obtained nanopowders, and also the technological virtues of the method GDS (very low expenditure of energy, has one stage, ecological cleanness) do a line-up an oxide - metal-oxide quite acceptable for a commercial production.

The influence of basic macroparameters of a plume (fuel and oxidizer concentration, metal particles dispersion) and also thermal structure of the combustion zone on disperse and phase characteristics of the combustion products have been investigated by experiment for aluminum. For the definition of temperatures of condensed and gas phases in combustion zone the spectral methods were employed and for the analysis of the combustion products the disperse and x-ray- methods were used. It is shown, that nanopowder of alumina (average size of particles 0.06-0.07 microns,  $\gamma$ -crystal phase), which properties depend little on variation of parameters of synthesis, accounted for no less than 99.5 mass percents of the products.

For powders of the high-boiling metals, such as Fe, Zr, Ti it is proved the possibility of their gas-phase combustion (under the temperatures of gas and condensed phase in combustion zone, which is lower than temperature of the metal boiling) with formation of oxide nanopowders of these metals (average size of particles - 0.02-0.05 microns). Zr, Fe, Ti particles burn heterogenetically in two-phase plumes with a low content of oxygen in carrying gas flow with generation oxide particles, which sizes are of the order of particles sizes of the initial fuel. Increase of oxygen concentration in particles dust clouds of these metals (more than 40-50 %) result in sharp increase of yield nanopowder fraction of the combustion products, i.e. intensification of gas-phase reactions.

This work was supported by the Ministry of Education of Ukraine and partially by INTAS under grant No. 96-2334.

### APPLICATION OF A RESTORED IRON POWDER FROM ROLLING SCALE AND DISPERSIBLIS PIG-IRON FOR MANUFACTURING A CONSTRUCTIONAL MATERIAL

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Probable use of a restored powder for manufacturing sintering constructional steels of structure iron - carbon, iron -chrome -carbon. Has been investigated. An initial iron powder was received by the combined restoration rolling scale by dispersed pig iron in a hydrogen atmosphere [1].

There has been graphite ГК-3 as an aliment, which entered in mixture at the rate of 0,2; 0,4; 0,6; 0,8 carbons in a material. The ferrochrome of the mark ФХ 800 contained 66,7 % Cr and 8,14 % C was entered in such amount, that the chromium steel contained 1, 3, 5 and 7 % Cr. All technological operations are investigated: preparation mixture, pressing, sintering in order to develop optimum technology of deriving sintering structural part. Initial mixtures were pressed under the pressure of 400, 500, 600 and 700 МПа. Samples were being sintered for 2 hours in a hydrogen atmosphere in laboratory installation of a flowing type with the temperature of 1000 °C for iron - carbon and 1150 °C for iron -chrome -carbon csteels. During sintering 1-2 % volume shrinkage of powder materials happens and depends up on pressure of pressing and contents of carbon in mixture. With growing of pressing pressure volume shrinkage example is reduced. Samples containing a smaller amount of graphite, are subjects for greater shrinkage. The tendency for growing of examples is observed for iron - carbon powder steels. Especially it is appreciable for want of introduction 7 % Cr.

Hardness and breaking strength were investigated. According to our results use of the restored iron powder obtained by combined restoration rolling scale by dispersed pig-iron in a hydrogen atmosphere, ensures increase of hardness in 1,2-1,3 times, strength in 1,3 - 1,5 times on a comparison with structural part received on basis atomized powder BPMP.

[1] Рослик И.Г., Острик П.Н. Получение восстановленных железных порошков из прокатной окалины и дисперсного малокремнистого чугуна // Теория и практика металлургии.-1998.- №2.- С. 36-37.

# REGULARITIES OF STRUCTURE FORMATION IN IRON POWDERS IN THE ROW "PRODUCTION - COMPACTING - SINTERING"

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Certification of the structure of iron powders produced by air dusting of high carbon melt on different technological stages of their production after compaction and isothermal sintering in hydrogen has been done. The following features were established:

- Formation of raw powder particles at atomization stage is controlled by active gas extraction from solidificated drops, by clash of drops and particles, also by effect of thermal stresses on interface between particles surfaces and metallic core.
- Phase composition of raw powder includes oxides  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$   $\alpha$ - and  $\gamma$ -phases. Quantity and dispersivity of the phases increases with decrease in particle size.
- Formation of grain structure of the iron powder occurs at the stage of reduction annealing in hydrogen with formation of low-energy grain boundaries (twin, facet or other types) and it is characterized by inhomogeneity in grain size.
- Pressing to grain porosity  $\theta=10\%$  promotes formation of point and line contacts between particles and causes small strain hardening.
- Reduction in size of grain and pores structure is observed in the process of nonisothermal sintering of air-atomized iron powder compacts occurs as the result of intra- and interparticles primary recrystallization at  $T=0,55 T$  melting. Growth of grains and pores occurs at temperature near to  $0,7-0,8 T$  melting due to grain growth. Simultaneously the grain shape, middle size of grains and pores, and also their size distribution are restored up to initial level in compacts. The phenomena was designated as "structural heredity".

The work was made because of financial support of Russian Education Ministry.

### PREPARATION MONODISPERSIVE SPHERICAL SILICA POWDERS

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Lately there was shown a possibility of preparation new ceramic materials (photon crystals) which may be a development basis of optical devices with improved spectral selective characteristics.

Development of such ceramic materials is connected with solving some complicated problems. The most important one is a development of methods of preparation ceramic powders with dimensions in the range 200-380 nm (a size of wave's semi-length of the seen light). The particles must have a regular spherical shape and be monodispersive ones.

In the work there are investigated synthesis processes of  $\text{SiO}_2$  powders by a sol-gel technique. Tetraethylorthosilicate (TEOS), ethanol, distilled water and water ammonia of high purity. After synthesis the powders were subjected to the thermal treatment in the temperature range 600-900 °C.

Studied is an effect of water and ammonia concentrations on a average particles size, determined is a range of values of the medium changing parameters where a synthesis of particles with the needed sizes is possible.

Prepared are spherical silica powders, the average particle sizes 200-400 nm and a variation 4-9 % of the average one. A variation 4 % maximum was achieved when fulfilling multistage building up of  $\text{SiO}_2$  particles.

Thermal treatment of the synthesized  $\text{SiO}_2$  powders results in changing their phase composition. X-ray phase analysis results testify that if a source material is in an amorphous state then after thermal treatment it transforms partially to small crystalline state. The amorphous phase makes somewhat 50 % (its quantity somewhat lowers with the temperature growth), the rest is a small crystalline  $\beta$ -cristoballit with crystallites sizes somewhat 5 nm. Results of measuring of specific surface and pycnometric particle's density testify that the particles are practically nonporous, their density approaches a theoretical one (2.25 g/sm<sup>3</sup>).

**MASS TRANSPORT INFLUENCE THROUGH THE GAS PHASE  
ON THE CONSOLIDATION PROCESS DURING SINTERING IN  
THE CHEMICAL ACTIVE ISOLATED GAS MEDIUMS**

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In works on sintering by Ya.I. Frenkel, B.Ya. Pines, Ya.E. Geguzin the principal attention was given to the process of interparticle contact area growth by means of diffusional mass transport.

Nevertheless B.J.Pines calculated according to avaporation and condensation mechanisms the neck diameter  $[x=f(t)]$  during spherical particle festbacken to the plane or each other. He obtained formula  $x^7 \approx t$  in the closed space conditions (it was assumed that all the atoms avaporizing from the surface condense into the neck). He also obtained relationship  $x^3 \approx t$  in real conditions of the flowing shield medium (part of the atoms does not condense into the neck). Thus a closed space in comparison with unclosed one provides increasing interparticle growth rate  $10^4$  times.

For the first time in the powder metallurgy practice we succeeded in realizing the closed space conditions using containers with a fusible gate for the purposes of sintering. On the basis of such self-contained containers authors worked out ductile powder chromium sintering technologies in the chemical active gas mediums, i.e. in the activated consolidation conditions.

Activated consolidation means an effective interparticle contact growth by means of intensifying mass transport through the gas phase with the simultaneous refining the matrix, grain boundaries, particle surfaces and pores of interstitial impurities and oxide film reduction.

The devised technology of activated consolidation conformably to obtaining the functional materials with maximum high porosity (about 90 - 95 per cent) on the basis of foam metals and knitted semifinished items gives especially good results. The devised method of activated consolidation of interfibre contacts by intensifying the substance mass transport through the gas phase provides not only the contact formation of high quality in such systems but also leads to increasing the substance deposition with the simultaneous course of the chemical and thermal process. The joint course of mentioned processes provides obtaining the high porous (about 95 per cent) functional materials with a high level of mechanical stiffness. Such materials can be used in the new and special fields of engineering as effective dampers and heat shield parts.

CONTROL OF STRUCTURE AND PROPERTIES OF LINING  
MATERIAL FOR HOLLOW CHARGES DURING FORMATION OF  
GREEN HETEROGENEOUS POWDER COMPOSITION

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The Composite heterogeneous powder material Copper-lead-graphite is one of the most effective for manufacturing of hollow charges commonly used for perforation of gas-oil wells. Livings are produced from powder mixture Cu(basis)-Pb(10-25%)-C(1-5%) by compacting, which allows demanded structure of the material, necessary strength and other properties.

Homogeneous distribution of components in the mixture during the blending is the first condition. The second one is providing for uniform porous structure when consolidated, as well as avoid in homogenitics of component distribution through the section of the part.

The main pole in the control of structure and properties of green parts is a choice of compacting scheme. The effective compacting schemes were elaborated taking into account the complex shape of the part (cone) and relatively then wall of cone. The stress state of the material compacted is considered. The construction of a press mold (die) for optimal compacting scheme of lining is presented.

The strength characteristics of as-prepared powder compositions depend not only on powder charge properties but also morphology of particles. Taking into consideration the mentioned factors, the powders selected consist of particles of suitable shape for good cohesion and slight deformation in required direction to form the uniform structure.

The manufacturing of powder livings is adjusted to supply the hollow charge in stead of forged copper linings. Such a substitution allows avoiding (a lack) pinching off of branched channels and increase the productivity of gas-oil wells.

### TRANSFORMATION OF PERMEABLE MATERIALS PROPERTIES IN THE PROCESS OF EXPLOITATION

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Porous permeable materials (PPM) made by powder metallurgy technique are widely used in various branches of national economy. The effectiveness of their application is based on combination of some hydraulic, capillary and physical-mechanical characteristics, determined correspondingly by structural and frame properties. To determine an optimum combination of the basic PPM properties there is proposed a dimensionless parameter  $\chi$ , derived from the expression  $\chi = \sqrt{k} \cdot \sigma_y \cdot S_v / d_{ep}$ , where  $k$  - a pore size,  $\sigma_y$  - specific strength,  $S_v$  - specific surface of the porous body.

We calculated values of the  $\chi$  criterion for porous materials to be used for various purposes. for filters of water preparation systems fabricated from binded metal gauzes is connected with filling pores with grains of a filtering backfill and sedimentation of the material surface that results in decreasing pore sizes and lowering permeability. Values of mechanical properties there with practically do not change.

For filter substrates used during recovery of synthetic diamonds, the change of the  $\chi$  criterion is stipulated by actively proceeding corrosive processes. Therewith a decrease of mechanical properties predominates the increase of permeability due to corrosion and the decrease of the wire diameter.

The criterion decrease of the  $\chi$  effectiveness for flame barriers is stipulated by proceeding corrosive processes. As a result of flame effect a part of summarized metal contact and therefore mechanical properties and permeability due to filling the bulk of porous area with corrosive products decrease.

# **THERMAL PROCESSES AND THEIR ROLE IN FORMATION OF DEFECT STRUCTURE OF MECHANICAL-ACTIVATED DISPERSED SYSTEMS**

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The fine defect structure (FDS) of dispersed systems largely determines properties of materials, received from them. Therefore an information on a nature and regularities of FDS formation on various external treatments of real systems represents both scientific, and practical interest.

In the presentation the nature of thermal effects which are developed on machining of solid states is considered. The attention is drawn to the fact, that the following of such processes is only taken into account, but practically is not included in mechanochemistry. The number of experimental results allowing to detect and to select of such phenomenon is listed. They also permit to evaluate their role in FDS creation of treated dispersed systems.

In a common case in mechanical reactor the next situation is realized: the local development of thermal processes in a zone of defects formation assumes heat transport on a chain: a zone of thermal process development - microparticle - dispersed system - operating units of crusher - external medium. Given off heat is directed to annealing of created activest defect states, to heating up of the dispersed system promoting as change of mechanical properties, and activation of interparticle interaction processes and interaction with an medium, heating up of the crusher and medium.

The role of regimes of processing (energy intensity of the crusher-activator, duration, capacity etc.), heat conductivity of units of a chain and some other factors in FDS creation of the treated system is considered. Some general conclusions can be drawn regarding radical necessity to take into account the thermal phenomena on consideration of the majority mechanochemical processes. .



# MECHANOCHEMICAL SYNTHESIS OF INTERMETALLIDS IN Ti-Fe AND Ti-AL SYSTEMS.

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The specificity of technology of mechanical alloying as non-equilibrium process consists in a possibility of obtaining of materials in metastable state. Therefore from the moment of the discovery (1983 year) the process of solid-phase amorphisation of alloys the interest to study of processes mechanical alloying is with speed increased. In most cases mechanotreatment of metals is carried out or in an air, inert atmosphere, or in an organic solvent. Substances anomalous behaviour at the its MCA in the water presence were long ago discovered but the nature of its phenomenon sufficient clear understanding are not of obtain yet. Kharlamov A. et al [1] was observed interesting fact on the water decomposition in the presence vanadium oxide (V<sub>2</sub>O<sub>5</sub>).

In the present report some results concerning singularities mechanochemical alloying of metal powders in water will be represented. The experimental results were obtained during a dispergation, in particular, titanium and mixture (Ti + Al) powders in planetary high-speed mill with metal drums and balls. It was established, that during a dispergation of a titanium in the presence of water the saturation a metal by hydrogen from a water are observed, in the one hand, and the saturation by an iron from balls in the other hand. Besides an oxygen in dispergated powder was just increased a little (with 1.2 up to 1.6 %).

X-ray method is shown, that a dispersgatio product represents itself an initial titanium, titanium hydride (cubic) and intermetallid TiFe<sub>2</sub>, but not TiFe, which formation may be more logical because of a surplus of a titanium. However phase TiFe occurs only after thermal exposure of a dispergated material. The presence oxide phase of a titanium in a product milling was not revealed.

[1] A.Kharlamov, V.Zazhigalov. Peculiarities of Properties of Mechanically

Activated in Various Media Oxide Vanadium.//NATO ASI Advances and  
Challenges in the Catalytic Activation and Functionalisation of lights

Alkanes; May25-June7, Faro Portugal, 1997, p.43-45.

## ALLOYING POWDER ALLOYS FOR a GAS-THERMAL SPRAYING

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The perspective systems of alloying for obtaining powder alloys from granules and also method of spraying of molten metal by air and high-pressure water, intended for a gas-thermal spraying of functional coatings are determined. The technological characteristics of powder alloys of systems Fe-Cr-Al-Si-C, Fe-Ni-Cr-Al-Si-C, Fe-Ni-Zr-Si-C, Fe-Mn-Cr-Al-Si-C, Fe-Mo-Cr-Si-C, inclusive as hardening phases carbides,  $Me_3C$ ,  $Me_7C_3$ ,  $Me_{23}C_6$ , MeC and silicides in quantities till 20 - 25 % are studied. The technological schemes of manufacture of alloys depending on alloying and such as a hardening phase are selected and are optimized. For alloys containing carbides MeC, at their manufacture it is necessary to prefer granular metallurgy with consequent fragmentation, which is most effective. The defining effect of aluminum on shaping of surface oxides, defining morphological characteristics of powder alloys is shown. The alloying by aluminum in quantities from 0,5 up to 3,0 %, microalloying by a titanium and boron, and also modification by calcium and rare-earth metal, allows to receive a broad band of morphological characteristics of powder particles, to lower a pollution of alloys by parasitic impurity and to achieve a content of oxygen in a powder no more than 0,2... 0,3 %. It is marked, that the powder alloys containing eutectic, during a gas-thermal spraying undergo significant modify structures, connected with processes of a remelting, overheat, solid-phase interaction, that reduces in significant redistribution and modification of a phase composition. At development of such alloys it is necessary to optimize a content of such elements as carbon, boron, silicon, which one during a spraying pass in solid solution, reducing a plasticity of a die, and also promote increase of a porosity. The shaping of structure occurs by all known mechanism of hardening, including by dispersion hardening, that determines high heterogeneity of coatings, the hardness, which one is differ from hardness of a powder.

**Research of Cr-Ni-Al-Y System  
Alloys with the Purpose of Creation of Wear and Heat  
Resisting  
Powder Materials.**

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The given work is devoted to study of Cr-Ni-Al-Y system alloys with the purpose of reception of a material with high both wear and heat resistance and to develop of the material manufacturing technology by powder metallurgy methods.

The search of optimum structure was fulfilled with using of cast alloys received by methods of electroarc and induction melting in a protective atmosphere. The specification of the Cr-Ni-Al system phases equilibrium was carried out, and also the influence of the yttrium additives on formation of phases and their structure was investigated.

The investigated alloys were located on the ternary diagram through which had been carried out from a point, appropriate to eutectic structure in Cr-Ni system (52.5 nuc. % Cr), and taking place so, that the parity  $0.019X_{Cr} + 0.0142 X_{Al} = 1$  was fair, where  $X_{Cr}$  and  $X_{Al}$  is nuclear concentration Cr and Al in observed alloys. The appropriate polythermal through was constructed with help of the researches executed by methods of differential thermal, metallographic and x-ray analyses. It was established, that at concentration of Al up to 4.4 nuc. % in cast alloys cooled with rate  $\approx 1000$  K/s  $\gamma'$ -phase is not formed, and the observable eutectic has similar morphology as one formed in binary Ni-Cr system. Four-phase eutectic equilibrium  $L \leftrightarrow \alpha + \beta + \gamma$  has a place at  $1290 \pm 5^\circ\text{C}$ . Four-phase equilibrium  $\beta + \gamma \leftrightarrow \alpha + \gamma'$ , occurring as a result of contact of the conode triangle of peritectic equilibrium  $\beta + \gamma \leftrightarrow \gamma'$  with surface of phase border  $(\beta + \gamma)/(\alpha + \beta + \gamma)$ , has a place at temperature  $980 \pm 5^\circ\text{C}$ .

The powder alloys of Cr-Ni-Al-Y system were received by a method of hot dynamic pressing and sintering. The powders of Ni, Cr and Al were mixed up in ratio, which provided formation of ternary eutectic  $(\alpha + \beta + \gamma)$ . Yttrium was entered as chemical compound which dissociated at the sintering temperature with formation of yttrium in an atomic condition.

Metallographic and X-ray analyses, test of friction properties and test of wear and heat resistance of received powder alloys were carried out.

## TREATMENT OF AN ALUMINIUM MELT BY DISPERSED TITANIUM NITRIDE PARTICLES

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Isotropic properties and ease of fabrication are the most important advantages of particle reinforced materials. Such aluminium-based materials possess fairly high specific strength, stiffness and wear resistance.

The two predominant techniques for the fabrication of particle reinforced materials (PRM) are powder metallurgy approach and molten metal processing approach. The latter offers an advantage of lower production costs due to the utilization of casting technology with a reduced number of processing steps. For this approach to become a technique of mass production of aluminium-based PRM sufficient wetting of the ceramic particulate by the melt must be secured.

The technique developed for the introduction of dispersed particles of refractory compounds with the aid of fluxes into melts enables to obtain a high degree of absorption of the solid phase and its uniform distribution within the melt. On introduction of the particles from the flux into the melt the following occurs: a local temperature increase, the dissolution of the protective oxide film at the metal-flux interface, the wetting of the particle surface by the flux and the transfer of the particles to the melt. The reverse process does not take place owing to the fact that the reaction between aluminium and the flux occurs completely.

During solidification the dispersed particles form nuclei on which an intermetallic phase grows. The latter, in turn, acts as a nucleus for the growth of aluminium dendrites.

Various techniques for pre-treatment and introduction of the particles, as well as various particle types, were tested out. In comparison to the treatment by zirconium a three-fold decrease in the aluminium micrograin size was achieved (from 145  $\mu\text{m}$  to 46  $\mu\text{m}$ ). In the case of application of titanium nitrides as a dispersed reinforcement a maximum effect was attained.

It was established that in the alloys obtained a change of mechanisms for deformation and failure occurred due to the formation of complex intermetallic phases and the presence of the dispersed particles.

**PECULIARITIES FOR LIQUID-PHASE  
SINTERING PROCESS OF  
DIAMOND/METAL COMPOSITES  
(DIAMOND/TiC/METAL MELT)**

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The mathematical model of liquid cuff between two spherical particles (diamond and/or TiC) has been developed. The algorithm for estimation of the liquid cuff shape has been created. The forces acting on the particles have been calculated depending on their size, distance between them, cuff volume, capillary characteristics of the diamond/TiC/metal melt (Cu-Sn-Ti) system..

The experimental data on the diamond/TiC/Cu-Sn-Ti composite shrinkage in dependence on these factors have been represented. Experimental data have been compared with estimated ones.

Some peculiarities of liquid phase sintering mechanism have been considered.

# THE SERVICEABILITY AND WEAR RESISTANCE OF THE METAL -DIAMOND COMPOSITE REINFORCED BY THE ALUMINIUM BORONCARBIDE

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The main tasks of the adding of the high-hard particles to the material used for making diamond tools are the following: the first, to increase the operational properties, and the second, to decrease the prime cost of these tools.

The question of interest was to determine the role of the high-hard compounds  $AlB_{24}C_4$  and  $Al_3B_{48}C_2$  as the second abrasive in the tool materials containing diamond.

It was ascertained the fine inclusions of the aluminium boroncarbide promote to increase the serviceability of tool up to 2.3 times and the operational stability up to 3 times (Fig. 1). The test was the grinding of the glass.

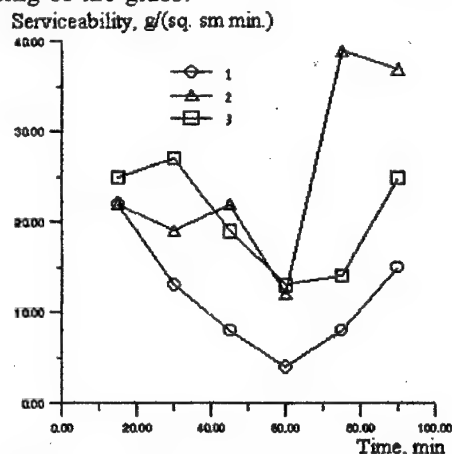


Figure 1. Dependence of serviceability of tool pieces on test duration.

- 1-  $K=12,5\%$ , A20/14, M2-01;
- 2-  $K=12,5\%$ , A20/14, 40 vol % of clasp of aluminium boroncarbide, 10/7;
- 3- the same as 2, the strength of clasp of pieces on counter-object up to 20 %.

### PECULIARITIES OF LIQUID PHASE SINTERING OF FINE PARTICLE COPPER-IRON BLENDS

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The liquid phase sintering of fine particle Fe-30%Cu metal powder blends up to 1130°C was investigated. The microstructure evolution of fine grain composites during sintering and during heat treatment of high density specimens were investigated too. The metal powder blends with particle sizes less than 0.5 mkm were prepared by mechanical alloying technique. Because of fine particle sizes of the initial metal blends the shrinkage of compacts were observed at all temperatures of sintering, the value of shrinkage at the temperature 930°C was 17,9%, it was 26% at the temperature 1130°C.

The microstructure of solid-state sintered composites was practically identical for all specimen treatment conditions and featured a high degree of dispersity and uniformity. Iron and copper grains had an elongated form, the grain thickness was about 0,1 mkm. At the temperature 1,130°C a very fast roughness of the microstructure took place as during sintering powder blends as during heating of the high-density specimens. Iron grain sizes were decreased because the liquid copper penetrates along the iron grain boundaries. The secondary rearrangement was observed. The grains acquired a form close to spherical, then they grew in size to 10-15 mkm. The mechanism of microstructure transformation was discussed. The rearrangement in the high-density materials during the initial liquid phase sintering stage to consider is impossible.

The fine grain Fe-30%Cu materials treated in solid-state have high hardness and good conductivity after hardening. Their hardness reaches 2200 MPa. These characters impair immediately when the copper liquid phase appears.

The fine grain Fe-Cu composites will be applied as a material for contacts and as a matrix of diamond instrument.

## STRUCTURE AND PHASE CONTENT OF HOT FORGED COMPOSITE MATERIAL OF BRONZE-IRON-GRAPHITE TYPE

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Studied bron - iron -graphite material is intended for electrocontact plates of pantographs of DC electric locomotives. The initial charge is mixture of copper, tin, iron and graphite powders. The quantity of tin in such charges is recommended to be chosen in the range of 6 to 12 %, iron 3 to 12 % and graphite 2 to 15 %. For synthesis of the material the method of hot forging is chosen. The technological process includes following basic operations: pressing of initial powder mixture into blanks with porosity 20 ... 30 %, heating of blanks in hydrogen to temperature of 850°C and forging of blanks with porosity of 3 ... 4 %. For studying the material the methods of X-ray diffraction analysis, X-ray phase analysis and X-ray mikroanalysis were used.

It was established that already during heating of blanks to said temperature there take place the formation of Cu-Sn alloy, the traces of copper and tin phases in pure state after heating were not observed. The relief of alloy particles looks like characteristic for liquid-phase sintering which may be explained by liquid state of some quantity of  $\beta$ -phase at 850°C. It means that forging proceeds at the presence of liquid phase. Fe-Sn phases were not detected even in local state. Copper oxides being present in copper powder does not reduce.

In forged material bronze grain relief has strip character, that, most probably, is connected with formation of many doubles in solid solution of Cu - Sn. The qualitative evaluation of diffraction maxima broadening, belonging to solid solution of tin and copper, in heated samples with and without exposure of heating temperature leads to the conclusion that in first samples there is much more concentrational heterogeneity of tin distribution in copper. Forging without changing phase content of the material, influences the microstructural characteristics of phases, and leads to additional dislocations. The formation of such microstructural imperfections may promote hardening of the material. At the same time, hot forging promotes aqualization of concentrational heterogeneity of content.

High density, prescribed phase content, heterogeneous structure of hot forged material provide reception of physical ( $\rho=0,223 \dots 0,259 \mu\text{Ohm.m}$ , HB 68 ... 72), mechanical ( $\sigma_{\text{bend}} = 240 \dots 252 \text{ MPa}$ ), and tribotechnical (friction coefficient 0,15) properties required for reliable use of electrocontact plates.



# WEAR RESISTANCE OF IRON-GLASS MATERIAL UNDER CONDITIONS OF DRY AND BOUNDARY FRICTION

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This work studies the characteristics of wear and friction of the same pair of powder hot forged material under conditions of dry and boundary friction to determine the regions of loads and sliding speed at which the material is efficient.

Material of Fe + 5 % glass + 1 % graphite content was obtained by the method of hot forging followed by heat treatment (hardening and quenching). Powder material density was 7,05 g/sm<sup>3</sup>, hardness after heat treatment was 50 - 60 HRC.

Wear test were carried out by means of friction machine operating according to scheme shaft-shell under conditions of dry friction using industrial oil 20 as a lubricant. During wear the load was raised by 2,5 MPa step-by-step, friction force and friction coefficient being registered automatically. Sliding speed was 0,4 to 4,4 m/s, linear wear was determined with the accuracy of 10<sup>-8</sup>. At friction with lubricant the wear was evaluated according to mass loss of a sample and a roller.

It was stated that under conditions of dry friction the material has high wear resistance ( $< 10^{-8}$ ) at speed of 0,4 m/s to the load of 40 MPa with friction coefficient of 0,4 to 0,6.

Further increase of sliding speed is accompanied by sharp decrease of wear resistance; the higher sliding speed the lower loads are required for catastrophic wear. The use of lubricant lowers the friction coefficient to 0,02 - 0,15 and expands the region of high wear resistance from speed of 0,4 to 2,0 m/s and under load up to 30 MPa. On the base of results of structure investigations, X-ray phase analysis of a material and friction surface as well as study of microgeometry of friction surface we described the mechanism of iron - glass material wear.

The data obtained allow to recommend an iron - glass material for production of seal rings in tractor running system by the powder metallurgy method.

# DIFFUSION MIDDLE TEMPERATURE SYNTHESIS OF NICKEL-PHOSPHORUS ALLOYS

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The interest to alloys of the nickel-phosphorus system has increased with obtaining the amorphous alloys on their basis, application phosphorcontand of solders, plotting the corrosionstable covers. A main method of obtaining of nickel-phosphorus alloys is the method to electroless chemical restoring by the hypophosphite from water solutions of nickel salts. The powders produced are polluted with oxydes and phosphates. The self-prohagating high-temperature synthesis method is deprived of these disadvantages, but demands the appropriate equipment.

Earlier [1] the method of obtaining of the copper-phosphorus alloys was described. It consists of phosphorus diffusion into copper powder at temperature of 200 -250 °C and subsequent homogenization the alloy the heating with an exposure at temperatures from 550 -650 °C. The same method was used by us for obtaining the nickel-phosphorus alloys. As is known, a temperature of melting an equilibrium of Ni-Ni<sub>3</sub>P eutectic is of 870 °C.

The powders of red phosphorus and of nickel electrolytic during two hours were mixed in the mixer, then the mixture was pressed into preforms of 0,5 kgs. The last ones were put in to the furnace which was warmed up to 500 °C in an atmosphere of hydrogen and were maintained within two hours. A significant loss of phosphorus were observed. Further the temperature was increasing up to 800 °C at the heating speeds of 15 °C per miute with an endurance one hour. The sintered preform was cooled with the furnace together, then was grinded or remelt for the temperature of 1000 °C. The loss of weight at the sublimation of phosphorum is 0,3-0,4 wt.%. The phase structure contains Ni and Ni<sub>3</sub>P.

The investigation carried out confirms the mechanism of interaction the nickel with phosphorus consists in the diffusion of phosphorum into the nickel grain at the primery with Ni<sub>3</sub>P obtaining and subsequen contact melting with the Ni-Ni<sub>3</sub>P eutectic obtaining. This mechanism was proposed by [2,3] former.

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# THE WEAR RESISTANCE AND SOME PHYSICO- MECHANICAL PROPERTIES OF THE HOT PRESSING OF THE COMPOSITE MATERIAL BASED ON THE HARD - MELTING BASE.

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The production of the antifriction materials for the friction units operating at possibly high pressures and speeds without forced lubrication is of great interest. It is known that the composites - systems high-melting compound-metal-solid grease as such materials are the most perspective.

The present work is dedicated to the study of the structure peculiarities and some physico-mechanical properties in a number of systems  $\text{Cr}_3\text{C}_2$  - Ni - P - C,  $[\text{Cr}_3\text{C}_2 - \text{Cu}]$  - Ni - P - C,  $[\text{Cr}_3\text{C}_2 - \text{bronze}]$  - Ni - P - C.

And the investigation of the processes for the material seal on ordinary sintering and hot pressing has been carried out.

The dependence of the relative density of the hot-pressed samples on the temperature, time, and applied pressure was established and optimum conditions for the material production were chosen.

The hardness, the bending strength, compression strength limit, wear resistance of the obtained composites have been determined.

The dependence of the friction coefficients on the friction speed and pressure under the dry lubrication conditions has been established and the direct correlation between tribotechnical indices and the strength properties was not found.

The mechanism of the composite wear and destruction during the friction without grease feeding in the contact zone in the air together with thermotreated steel 45 (HRC 45-48) and hard alloy BK 15 (HRA 90) on the scheme bushing-shaft within the load interval of 0.2 - 1 MPa and at the speed up to 30 m/s exclusively has been investigated.

The tests performed have shown that in a number of materials the relative wear resistance of the composition  $[\text{Cr}_3\text{C}_2 - \text{bronze}]$  - Ni - P - C is by 3 - 5 times higher than in case of the standard hard alloys.

**CHROMIUM-COPPER PSEUDOALLOY  
PREPARED IN AN INDEPENDENT ACTIVE GAS MEDIUM**

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Processes have been investigated, connected with activation of chromium-copper pseudoalloyed compositions during the sintering under an independent active gas medium.

It was found that surface powder refining of initial metals made under above conditions, leads to a decrease of wetting angles.

The sintering method to be proposed of powder composite systems that have an insufficient degree of wetting ability, under an independent gas medium will yield materials which are impossible to produce under other conditions.

Materials prepared by this method are suggested for the in new and special areas in the form of electrical or engineering products.

## NEW FERROCOMPOSITE MATERIALS FOR PERSPECTIVE

### APPLICATION IN ELECTRICAL ENGINEERING

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The work aimed at investigation of properties and possible application of new metal powders, known as ferrocomposites (FCs), having various combinations of magnetic, electric, mechanical, and thermic properties. They are the conglomerates comprising two or more constituents, one of that is a magnetic phase dispersed in the matrix of dielectric or semiconductor material.

Under consideration are six groups of materials for application at frequency range up to 5 MHz. The new progressive technologies of their production were developed. Their base is the methods of power metallurgy that permit to obtain products having required properties and any complicated shapes. Comparative values of specific loss of materials at different operational conditions (frequency, induction, temperature) are presented. Of particular value are FCs based on metal powders with improved properties and ferrite-cermetes.

Today, the FCs find a wide use in manufacture of chokes for power devices working at frequencies above 50 kHz, resonant inductance coils, differential EMI chokes, inductor coil chokes, noise filters, SMPS inductors, electric transformers etc.

The use of FCs permits to reduce the size of devices, improve their characteristics, raise the efficiency as well as to cut their prices and serve to better protection of environment from EMI noise pollution.

Powder composition	$\mu_i$	Bs, G
Molybdenum permalloy 80N-2M	14...500	7000
Permalloy 50N	60...200	15000
AlSiFe «Sendust»	60...125	11000
Sprayed iron	22...90	9000
Powders of amorphous alloys, 2HCP and 71KCHP grades	22...90	4000
Ferrite-cermetes	14...140	12000

TECHNOLOGY OF OBTAINING OF HIGH-STRENGTH  
WEAR-RESISTANT COMPONENTS OF HEIGHTENED  
DIMENSIONAL ACCURACY FROM LOW-ALLOY  
POWDER TRPEP STEELS

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Manufacturing of cutting electric tool requires technology of quantity production of parts for the drive possessing high wear resistance, strength to variable loads and high dimensional accuracy. The conventional technology of powder metallurgy can not be utilised, as at final stage of manufacturing during sintering and the heat treatments vary the sizes and geometry of articles.

In Republican Engineering Technical Centre of Powder Metallurgy (RETC PM) was designed the technology, protected by the patent of Russian Federation, of obtaining of articles which possess heightened dimensional accuracy, applicable to 9-10 quality, high strength and wear resistance. The articles were produced due to combination of operations of calibration and hardening at final stage of manufacturing. To combine operations was allowed thanks to the high plasticity of austenite and its high stability to precipitation due to decrease of points of martensite transformation  $M_s$  and  $M_f$ .

The technology of manufacturing of articles consists from: preparation of multicomponent mixture, pressing, preliminary sintering, repeated pressing, final sintering, calibration combined with hardening, tempering with impregnation in oil.

The technology realised on manufacturing of part "«Link" for the drive of electric saw "Master". The reached dimensional accuracy of width of axial slot was  $11^{+0,043}$  mms and deviation from parallelism of working edges of link on length of 100 mms no more than 0,1 mms at hardness of material 48 ... 52 HRC.

The possibility of application for powders of Ferro of the marks was investigated: PGRV 3.200.28, ASC 100.29, Distaloy AE. It was shown, that the purity of powder, except for the other factors, influences on quantity of carbon in steel. High strength up to 1100 MPa and the hardness up to 56 HRC provides obtaining of structure of massive martensite, and the subsequent tempering at 180 °C, combined with impregnation in oil, creates the good reasons for operating of article in conditions of dry friction.

### RESEARCH OF PROPERTIES OF MULTICOMPONENT SYSTEMS ON A COPPER BASIS POWDER SINTERED MATERIALS

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Now there is a tendency of the further extension of the nomenclature of powder items, used in mechanical engineering, that is connected to relative simplicity of technology, decrease of losses of metal in a shaving, absence of additional processing for want of maintenance of required quality of items. By the purpose of the present operation was learning possibility of substitution of details «ring of the synchro» received by turning processing of brass pipes preparations from a powder sintered material of similar structure.

Powder of a multicomponent alloy on a copper basis, with dissolved zinc, manganese, aluminum, iron, nickel, silicon, lead, received on aim of gas dispersion. The natural and running characteristics of an obtained powder of a brass and mixtures with the various contents of a brass and iron powder were investigated. The influence of a mode of sintering on the mechanical characteristics of powder materials, and also durability of sintered details «ring of the synchro» was studied.

The following production process of preparations in exchange of traditionally used turning processing of pipes is offered: production of a powder of a brass by nitrogen dispersion, preparation of powder mixture, consisting 60 % of brass, and 40 % of iron powder, pressing with pressure 700 MPa and sintering in an atmosphere of hydrogen at the temperature of 950 °C within 2 hours.

### OBTAINING WELLFORMING IRON POWDERS BY ROLLING IN ROLLING MILL

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The wellforming powders of iron as result of processing of a product carbonthermal restoring of ore «Blue Dust» concentrate (India) containing 1,5 wt.% oxygen and 0,2 wt.% carbon, the concentrate subjected consequent gas-thermal restoring ( $O_2$  - 0.2 wt.%, C - 0,02 wt. %) are obtained. In an offered research technology used earlier for fragile materials is approbated [1,2].

The comparative characteristics of powders after grinding by vibration mill and by rolling mill are obtained. The values of spend energy in the time of receipt of standard powders in both case are calculated.

The economic feasibility to receive of standards iron powders treated by rolling mill, and as overlapping of processes of grinding in a rolling mill with grinding in a spherical mill at the stage of finishing processing is shown.

From obtained powders the strips were rolled and tested shearing strenght in a grin state. The durability of strips is 13,5 - 15,5 kg/mm sq.

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**SEMINAR K.**  
**FUNCTIONAL GRADED MATERIALS**

**311-322**

## PRODUCTION OF GRADED CERMETS.

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The FGM concept provides degrees of freedom, previously unavailable, for designers of material systems and illustrates the late tendency to custom-design materials for specific applications.

Conventional approaches to produce graded cermets are based on a gradual change of the ceramic-to-metal ratio throughout the material. The desired gradient may be achieved by superposing layers of powders that have different ceramic-to-metal ratios followed by HIP or HP. An alternative approach is to sinter superposed layers of ceramic powders that have different rates of sintering and consequently generate a porosity gradient, followed by liquid metal infiltration. The main disadvantage of the first approach is its elevated production cost. The second approach yields composites in which significant deformation takes place during densification of the superposed layers that have different rates of sintering. This approach allowed us to obtain small size (20x20x10mm) graded parts based on the  $\text{TiC}_x\text{-Al}$  system. The properties and structure of these samples will be presented.

We have recently put forward a novel approach for the production of graded cermets in which the gradient is generated by changing the properties of the metal phase during infiltration and not merely by a change of the ceramic-to-metal ratio. This method was actually applied to  $\text{TiC}$  ceramics infiltrated with molten  $\text{Fe-C}$  alloys.

The titanium carbide phase has a wide range of stability that extends from  $\text{TiC}_{0.48}$  to  $\text{TiC}_{0.98}$ . Thermodynamic calculations have shown that the interaction between sub-stoichiometric  $\text{TiC}$  with steel causes carbon to transfer from the melt to the carbide, thereby increasing the carbon content of the former and depleting that of the melt. The composition changes in the metal phase induce microstructural and property changes that can be used to generate a graded ceramic-metal composite.

This approach allows reducing significantly the deformations that occur in graded samples, produced by conventional methods, by focusing on the  $\text{TiC}_{0.8}$  to  $\text{TiC}_{0.98}$  ceramic composition range. SEM examinations of the metallic component in the 'as infiltrated' graded cermet revealed a pearlitic structure on the  $\text{TiC}_{0.98}$  side and a ferritic structure on the low-carbon carbide side. At mid-height of the samples, a gradual change of the pearlite-ferrite ratio was observed. Thermal treatment affected only the pearlite-containing region, transforming its metallic component into martensite. The hardness of the graded samples increased from 900 HV to 1500HV along the sample.

RESEARCH OF CORROSION RESISTANCE AND INFLUENCES  
OF MASS TRANSFER PROCESSES FOR THE MECHANICAL  
CHARACTERISTICS OF POWDER FGM BASED ON THE SYSTEM  
FE - CR - NI - MN - C

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Recently interest to use FGM steadily grows on the basis of powder materials in various areas of mechanical engineering. In particular it concerns FGM, which main function - stability in the various oxidizing environments.

In operation the system Fe - Cr - Ni - Mn - C obtained by a method of single cold pressing and sintering is investigated FGM. For its obtaining the powders of iron, nickel, ground down powder ligatures iron - chrome and iron - manganese, and also graphite as carbonaceous component were used.

The material is constructed in such a manner that the functional load is a surface part, which chemical structure is similar to chemical structure of powder corrosion-proof steel Cr18Ni23. From one surface to other the amount of alloying elements falls, for want of it the part of nickel is substituted by manganese. A basis of a material is the constructional powder steel Cr8, imparting to a material as a whole high durability.

In operation the FGM corrosion resistance in various points of its volume distinguished from each other on chemical structure is investigated.

The influence of processes mass transfer and volumetric diffusion on hardness FGM in various points of its structure is investigated too.

# **BIOCOMPTIBLE GRADIENT CERAMIC COATINGS FOR THE METAL IMPLANTANTS**

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For the acceleration of the osteointegration processes of the metals implants we deposit on their surface the biokompatibile ceramic coatings on the basis of hydroxyapatite [HA] [1,2]. However such coatings have a certain deficiency connected with the absence of the necessary strength characteristics for a such kind of the implant. That's why it actual to create the coatings having beside biological compatibility the necessary strength and springy-elastic properties.

We have developed the method of the receiving of the new biocompatible coatings with gradient structure over width on the titanium substrate [3]. The essence of the developed method is in plasma coatings deposition with beforehand given supply of the powder consisting of two components ( oxyde aluminium and hydroxyapatite ) in the process of the deposition. It's showed that the received gradient coatings are the mixture of the crystals of  $Al_2O_3$  and HA, the concetrations of which change over the width. The topological investigation of the surface and the coating cross-sections was perfomed from which the chemical composition distribution over width was studied and found the absence of the chemical interakction between  $Al_2O_3$  and HA.

By regulation of the distribution of the initial components over the coating widths it is possible to set the phase comsposition and crystal sizes in the biocompatible coatings. In the process of etching in the solutions imitating the physiological ones it is found the formation of the pores having dendritic structure. The performed investigations show the possibility of the usage of the developed coatings in medicine particularly in stomatology.

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# **THEORETICAL AND EXPERIMENTAL PREREQUISITES TO MAKING A CONTROLLED TECHNOLOGY TO OBTAIN FUNCTIONALLY GRADED MATERIALS BY SHS METHOD**

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Modern functionally graded materials (FGM) represent a complex physico-chemical non-equilibrium object combining phases of different nature, compounds, components, alloys etc. Each element has its own thermodynamical, thermophysical, mechanical and other properties that makes impossible to use traditional techniques under consolidation of FGM. So among numerous methods to obtain FGM the SHS technology deserves particular attention. It offers a lot of advantages among which is a high output (mean rate of reactionary front motion is about 1-10 cm/s). But the main SHS advantage is first of all a possibility of consolidation subsystems with different properties in the context of realization of necessary thermal sintering conditions in each material element (layer). This possibility is due to revealing effects of high-energy self-localization under reaction front moving. Experimental study of individual reactionary front motion points to regular variations in temperature in each unit volume of material, that is stipulated by non-linear character of interactions of exothermic heat release and temperature activated processes (phase transitions, diffusion, sintering and heat transfer processes). So the problem of making a controlled technology to sinter FGM amounts to the elaboration of model views taking into account the set of all physico-chemical processes arising as a result of exothermic heat release and their collective role in forming the trajectory of maximum temperatures in the material volume. It supposes a possibility to control the trajectory of temperature changes under motion of reactionary front by lateral changing of thermodynamic and thermophysical properties of moulding or mixtures. By this it is possible to ensure the temperature needed for sintering of every particular physico-chemical system being in FGM set. It is necessary to note that the method allowing to predetermine the trajectory for changes of temperature front is, as seems, the only way to control properties and structure of material in irreversible hard-phase systems with non-equilibrium interactions.

# STRUCTURAL AND HYDRODINAMICAL AND HYDRODINAMICAL CHARACTERISTIC OF POROUS LAYERED METAL MATERIALS

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The porous materials from metal fibers (PFM) and powder (PPI) are in essence distinguished on gear form of their structures and properties. The distinction in nature of interpartial connections and structure of porous space PFM and PPI causes the considerable distinction in properties. PFM have high permeability, conductivity and strength. PPI differ by fine structure, low plasticity and porosity.

The interest is caused by porous fibro-powders materials, which largely preserve the positive PFM and PPM properties. However at present the effective ways of reception of such materials are not designed yet. Report submits the results of research of structural and hidrodinamical characteristics of porous layered fibro-powders materials from stainless steel.

The objects of research were the layers of separately and overleply formed and sintered powder and fibrous materials. Forming of layers was executed layer past layer sequential sedimentation of fibres and powder on special vibrator. On basis of made researches the dependences of permeability, average and maximal pore size of layered metal materials on porosity and ratio of particles sizes of powders and fibres are received.

The new material is developed, it preserves the positive properties as powder, as fibrous materials. For example, two-layered material with porosity of 55 % and ratio of sizes of powder and fiber particles is equal 1.2 in comparison with powder material differs by order greater permeability, and in comparison with fibrous material it has 2 times less of pore size.

# SLIP CASTING OF GRADIENT OXIDE COMPOSITES $\text{ZrO}_2(\text{Y}_2\text{O}_3, \text{CeO}_2) / \text{Al}_2\text{O}_3$

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The gradient ceramic materials are manufactured by various methods depending on the particular purposes in hand, such as width and quantity of layers, smooth or discrete change of structure on width, microstructural gradients.

The main objective of this investigation is to produce the gradient materials on the basis of the discrete layers of  $\text{ZrO}_2(\text{Y}_2\text{O}_3, \text{CeO}_2)$  and  $\text{Al}_2\text{O}_3$  founded from aqueous slips.

The  $\text{ZrO}_2(\text{Y}_2\text{O}_3, \text{CeO}_2)$  starting powders are produced with a combined method of high-temperature hydrolysis and sol-gel technology. The specific area of powders was changed from 14 up to 42  $\text{m}^2/\text{g}$  depending on composition. The specific area of the  $\alpha\text{-Al}_2\text{O}_3$  starting powder was 1,5  $\text{m}^2/\text{g}$ .

Any layer on the basis of  $\text{ZrO}_2$  obtained with slip casting has already a raw kind of the rather perfect microstructure which is not containing the anomalous of large grains and hard agglomerates. The interface of layers represents not equal plane, but complex cellular surface, that hinders the cracks expansion between heterogeneous layers. The intermediate layer somewhat inheriting the chemical structure of bounding materials forms on boundary of two layers. This intermediate layer lowers the stresses gradient on boundary. Such microstructure is responsible for the sintering up to density 98-99 % from theoretical in a narrow interval of rather low temperatures (1200 - 1400°C).

The castings walls width of the gradient material, with the total number of layers 21, were 1,5-2 mm after sintering, i.e. the average width of a layer was equal to 75 - 100 microns.

One from defects of slip casting is the complexity of a set of thick (more than 5-7 mm) layers under working with fine-grained powders similar used in present research, and forming high density castings. It is possible to use the hydrostatic pressing of more thin samples, folded of pile, when the occasion requires to manufacture the thicker gradient materials castings

**RESEARCH OF RADIANT ENERGY USE  
FOR OBTAINING INTERMETALLIC AND FGM BY  
SHS PROCESS**

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The SHS technology is of great practical interest owing to its high output. However, as well as any equilibrium process, it is practically referred to a non-controlled technology for obtaining materials with not easily reproducible properties. Initial conditions of exothermic reaction triggering is an important SHS technological process parameter, which determine properties of the final product. As a rule, under thermal and electro-physical initiating methods a spot ignition is observed, causing the formation of one or more spherical fronts. Radiant energy application is of interest due to a possible initiating of a plane reaction front, which is especially important at FGM obtaining. The formation of front reaction geometry was studied under synthesis of  $ZrAl_3$ ,  $ZrAl_2$ ,  $ZrAl$ ,  $ZrAl_3$  and their compositions with oxides  $Y_2O_3$  and  $ZrO_2$ . It was found that in all cases the formation of plane undamped reaction front was under way. In spite of high enthalpy of  $ZrAl$ ,  $Zr_4Al_3$  and temperatures over the fusing temperature for these compounds, there was no thermal explosion during the synthesis. At SHS front moving in intermetallic and oxide compositions, a periodic formation of different density layers took place. It may be caused by reducing the thermal wave length through diluting of reaction system with inert oxides of low heat conductivity. Under multi-component intermetallic synthesis in air medium we observe a secondary initiating of topochemical reaction of oxidation and formation of gradient structures with dense oxide ceramics which form on the surface.

The obtained results bring about a conclusion that the use of radiant energy for exothermic reaction triggering makes it possible to expand technological capabilities of the SHS process.



## THE INFLUENCE OF LASER TREATMENT ON FORMATION OF PROPERTIES OF FUNCTIONAL GRADIENT MATERIALS

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The data on obtaining and modification of functional gradient materials (FGM) such as thermal bimetals of the following systems: an amorphous coating / metal, (blends of oxides or alloys) / metal, two-layer coatings / metal (Si), bioceramics / metal were analysed. In obtaining thermal bimetal, consisting of some layers with different linear expansion coefficient, the original Fe-Ni alloy is metastable. While rapidly heating to 600 °C transformation of martensite into austenite without diffusion occurs and concentrational microexfoliation in  $\gamma$ -state remains. When laser treating heterogeneous alloys which have at a room temperature the body-centered cubic (bcc) and face-centered cubic (fcc) lattices, complicated structure with partial diffusion between layers forms. Conditions of obtaining system "fine-grained polysilicon—coarse-grained polysilicon—sapphire", "monocrystalline Si—porous Si" and amorphous layers GaAs (to 300 Å)/Cr Ni-P / Steel 45,  $ZrO_2$  / Si, Si-Cu-Pd / Ni-P / Cu have been described. While alloying titanium with laser beam it is advisably to use combined two-layer coatings (Cu,Ni)/ Ti and (Cr,Cu)/ Ti. As to laser alloying of Si, bilayer coating  $MoS_2$  / Fe is used. One should note some ways of forming films  $(ZrO_2 - CeO_2)$  / Mo and  $(ZrO_2 - Y_2O_3)$  / (substrates made of NaCl, Si (100), quartz) by means of laser evaporation of metals in the presence of ionic pencil of  $O_2$ . Conditions of obtaining system "bioceramics / steel or titanium" on the basis of hydroxyapatite Ca with laser beam have been described.

### DEVELOPMENT AND PROPERTIES OF SiC/TiB<sub>2</sub> MULTILAYERED COMPOSITES

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SiC-TiB<sub>2</sub> ceramics having a high enough level of mechanical properties cannot correspond to the demands for a high-temperature application because of their low corrosion-resistance. The corrosion-resistance of such system may be risen using a multilayered version. Herein as the outer layers the SiC ones are used. In this work the study was carried out to obtain the multilayered SiC/TiB<sub>2</sub> ceramics.

The two kinds of SiC powders were used:

- 1)  $\beta$ -SiC obtained from silica acid solution and saccharose; its specific surface was 15 m<sup>2</sup>/g, an average particle size was 0.1-0.2  $\mu$ m;
- 2)  $\alpha$ -SiC obtained using Acheson method; the particles size was 2-3  $\mu$ m.

The multilayered ceramics were obtained using a following scheme: a slip casting of thin SiC and TiB<sub>2</sub> films - a packet rolling - a hot pressing. The 5 mas.% B<sub>4</sub>C was introduced to both components as an additive which activated a sintering. The investigations of multilayered composites structure showed that at a hot pressing the dense TiB<sub>2</sub> layers (a porosity was 0-5%) formed at an insignificant recrystallization. The porosity of SiC layers depended on a kind of used powders, viz., it was equal to 5-15% in the case of  $\alpha$ -SiC and 20-40% for  $\beta$ -SiC, the grain size being ~10  $\mu$ m for  $\alpha$ -SiC. In the case of  $\beta$ -SiC the prismatic SiC grains with a thickness of 20-30  $\mu$ m and a length of 100  $\mu$ m and more formed as a result of resublimation. Herein the dense TiB<sub>2</sub> layers proved to be connected with each other by porous arch structures from the prismatic SiC grains. The mechanical tests showed that in the case of relatively compact  $\alpha$ -SiC/TiB<sub>2</sub> composites their bending strength (100-300 MPa) was lower than that of hot pressed one-phase  $\alpha$ -SiC and TiB<sub>2</sub> materials obtained from the components (400-500 MPa). In the same time the strength of  $\beta$ -SiC/TiB<sub>2</sub> composites proved to be higher than for the hot pressed one-phase components. It was equal to 600 MPa while the strength for hot pressed  $\beta$ -SiC was equal to 300-330 MPa. These results for the system may be explained by a high relaxation ability of the porous SiC arch framework in its layers.

THE MATERIALS POROUS GRADIENTS FORMED FROM  
METALS FIBROUS FOR HEAT TRANSFER SURFACES FOR  
EQUIPMENT WHICH FUNCTIONS IN BOILING REGIMES

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The results separates researches of intensity of heat transfer and critical heat flow for boiling of water in surfaces from porous gradients materials formed from metals fibrous represented.

Application of porous materials caked with heat transfer surfaces destined for equipment which functions in boiling regimes permit the attainment of considerable improvements of heat transfer parameters.

The series of models of heat transfer surfaces formed of metals fibrous are investigating. The models have the different porosity. The sections of porous surfaces have the different characteristics. The parameters of sections and their dispositions alternated. The thermophysical and hydrodynamical characteristics varied.

The series of experiments are investigating in boiling regimes on porous surfaces of models for free movement of water. The data findings are receiving the optimal characteristics of porous gradients materials. Their materials ensure simultaneously the considerable augmentation of intensity of heat flow and the augmentation of critical heat flow.

## PROTECTIVE COATINGS WITH GRADIENT TEXTURE ON METALS AND ALLOYS

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The layer columnar freezing diffusion alloying with round and needle, nano micro and macro inclusion texture was prepared by combination of methods of thermal treatment (TT), chemical thermal treatment (CTT) of composite electrolytic (CEC), galvanophoretic (GPC), plasma (PSC) coatings on Fe, Ni or Mo foundation, deposited on construction steel. The needed tribological properties generate in the process of preparation of composite structure and the following chemical thermal treatment, which form the required texture.

The characteristic of diffusion processes under interaction of structure elements CEC, GPC, PSC during TT or CTT and in the presence of eutectic transformation under melting and freezing was studied. The fact of increase of boron, chromium and aluminum diffusion in nickel matrix CEC was found. It connected with high deficiency of crystal matrix structure and presence of big interface borders between metal of coating and inclusion. In this case the ratio of interface diffusion increase. CTT of PSC increase the adhesion of coatings. They have hydro-abrasive resistance by an order less than common plasma and wear resistance in 2-5 times higher in the condition of face friction.

The working of model boron and chromium diffusion gradient coatings, based on nickel with powder titanium carbide and boride inclusion carried out in the conditions of dry friction and hydro-abrasive wear was shown in 1,5-2 times higher than boron steel 45, nickel and CEC nickel-boron. The optimal properties have the coatings with 22-25 % powders of particle size 28-50 mcm.

### NEW FUNCTIONALLY GRADED MATERIALS BASED OF FINE CERAMICS AS COMPONENTS FOR ENGINE

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Advanced structural ceramics based on nitrides and carbides are well known candidates for replacement of conventional metal parts in gasoline and diesel engines and gas turbines. They can also be used as bearings and wear parts. Also ceramic composites are widely investigated in order to improve mechanical, electrical and thermal properties of these candidates. Recently Funktionally Graded Materials (FGM) - composites with controlled electrical conductivity are replacing metal parts in special electrical and electronic devices what not only increases the performance of these components but also the range of applications for advanced ceramics.

Microstructure, electrical and mechanical properties of ceramic composites in the system  $\text{Si}_3\text{N}_4$ -TaN are studied to develop a new class of electroconductive material with a positive thermal coefficient resistivity. The TaN content was variable in the composite composition and was between 5 and 50 vol.%. It was revealed that the use of a coarse, non stoichiometric tantalum nitride powder as a second component of the composite, combined with the reducing (CO) atmosphere of the sintering process resulted in the formation of a chain type network of the electroconductive phase. The formation of a new phases such as SiC,  $\text{TaSi}_2$ ,  $\text{Ta}_5\text{Si}_3$ ,  $\text{TaC}_{0.5}\text{Si}$  and  $\text{Ta}_5\text{Si}_3\text{N}_7$  in the composite body during the sintering process was also recorded. A quite different microstructure was observed when the composite material was sintered in a nitrogen atmosphere or a fine TaN powder was used. These composites were characterized by a ring-type network of the conductive phase in the insulating matrix. The electrical conductivity of the manufactured composites strongly depended on the formation of a percolation network. A minimum quantity of TaN additive which protected in a good conductivity of the composite was established for 13.5 vol.%. The obtained electroconductive composite was characterized by a positive thermal coefficient of resistivity in a temperature range of 400-900°C. The room temperature mechanical properties of the developed composite were comparable to the mechanical properties of the monolithic  $\text{Si}_3\text{N}_4$  material.

The application of these materials as igniter rod devices of combustible mix in diesel engines is shown. The confirmation of high profitability from use of ceramic heaters in climate systems for automobiles is indicated.

**SEMINAR L.**  
**NANOCOMPOSITES**

**324-333**

## NANOCRUSTALLINE ALLOYS PREPARED BY MECHANICAL ALLOYING

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A review of experimental results of peculiarity formation alloys in the Fe-Zr-N, Fe-Ti-N, Fe-Al-N, Fe-Mo-N systems are given. The mixtures of elemental powders Fe-Me were mechanically alloying by high energetic vibrating mill in Ar and  $\text{NH}_3$  atmospheres. The process of mechanical activation of the mixtures of elemental powders iron and titanium was carried out in an  $\text{NH}_3$  atmospheres in two ways. The first method provided for carrying out the process of mechanical activation of the starting components in a hermetically sealed reactor in an  $\text{NH}_3$  atmosphere. Using a pressure gauge, the fluctuations of pressure within the reactor were measured during the process of activation. The second method consisted of constant forcing of  $\text{NH}_3$  through the reactor throughout the activation process. Mossbauer spectrometry, X-ray diffractometry and chemical analysis were used to study the kinetics formation metastable phases in Fe-Me and Fe-Me-N alloys obtained by mechanical alloying. The thermal stability of the powders have been investigated by differential calorimetry. It was shown that continuous passage of  $\text{NH}_3$  through the reactor during the process of activation contributes to obtaining higher concentrations of nitrogen in the alloy than in the case when the process is carried out within a sealed reactor. It was established that Mossbauer spectrum of the final product is quadrupole split doublet after milling the mixture of elemental powders Fe+25% Ti for 10 hours both  $\text{NH}_3$  and Ar atmosphere. An examination of the Mossbauer spectrum suggest that the spectrum similar sputtered amorphous Fe-Ti alloy.

With increasing the milling time (over 10 hours) in the  $\text{NH}_3$  atmosphere of the nitrogen content more than 1.6% and quadrupole split doubled was absent on the Mossbauer spectrum. Thermal stability of the metastable phases, depending on their nitrogen content, results in the formation of intermetallic compounds or nitrides.

High values of nitrogen and titanium concentrations in the mechanically doped iron were due to the formation of corresponding segregations, which in the course of subsequent high temperature annealing are transformed into equilibrium phases.

In this case, by means of mechanical alloying, it is possible to form alloys with a finely dispersed structure and a nonequilibrium phase, the grain sizes of which do not exceed a few nanometers. Such materials, known as nanocomposites, possess extremely high mechanical properties at both room and high temperatures. In the past few years there has been a growing interest on a new kind materials.

## **THE PRODUCTION OF NANOSTRUCTURED METAL COMPOSITES BY CHEMICAL DISPERSE METHOD**

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The chemical methods of production of nanostructured (NS) materials has the advantage of cheapness and high efficiency in comparison with traditional physics methods. The combination of precipitation from solution with following hydrogen reduction of sediment permits to obtain as an individual NS Fe, Ni, Co, Cu, W, Mo powders, as a various composition on base these metals. Structure and properties of NS metal composites, as a particle size and particle size distribution, phase composition, specific surface, morphology, can be regulated by means changing of production regimes (pH of solution, holding time and temperature of reduction).

The basic principles of mutual component influence in NS composites during formation were established and the mechanism of solid solutions formation for such systems was suggested. It has been shown, that the formation of NS composites is accompanied by structural relaxation, which accelerates greatly the processes of phases and alloys formation in comparison with traditional materials. A lot of attention was paid to singularities of a crystalline structure of nanocomposites, which depends dramatically from compositions and formation regimes. On a basis of obtained data a technological conditions, permitting to gain NS materials with a grain size 10-40 nm and narrow particle size distribution, are designed.



### **NANO-STAGE IN STRUCTURE DEVELOPMENT OF THE 'IN-SITU' COMPOSITE AL-SI ALLOYS**

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Studies on microcrystalline aluminium alloys for industrial application have been intensified for the last 15 years]. One successful method for achieving initial microcrystallinity is the rapid solidification from the melt. Good results both in quality and yield are obtained by one-wheel facilities. The thermal treatment of such alloys during and after hot-extrusion compacting leads to structures which are "in-situ" composite materials. It appears that a preliminary treatment (working or annealing) of the as-cast ribbons has a significant influence on the properties of the so obtained bulk microcrystalline aluminium alloys.

XRD and TEM studies were performed to monitor the solid solution decomposition and stages of structure development. The data on eutectic and under-eutectic Al-Si alloys show differences between the as-cast and beforehand-normalized specimens, which are compared after heat treatment at temperatures usual for hot extrusion. The observed unexpected difference can be explained with the appearance of intermediate nano-scale phases during the normalizing stage. These phases (silicon or intermetallics) may lead to a special mechanism of further structure development at high temperature processing.

The aim of our study is to reveal the mechanism of structural changes during the preliminary normalizing anneal and the final size and morphology of new phases – result of the supersaturated Al-solid solution decomposition.

It was found that nano-sized Si-particles with short interval of size dispersion are distributed randomly in the Al-matrix grains and during the high temperature treatment they help to achieve lower rate of phase coarsening and thus the initial microcrystalline structure can be preserved. Hence the hot extrusion processing could serve as a hardening thermal treatment, preserving high level of ductility for final forming of machine details.

**NANOCRYSTALLINE CERAMICS:  
STRUCTURE AND SIZE EFFECT.**

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Structure sensitive properties of nanocrystalline materials are determined by structure of grain boundaries or interfaces, as well as grain size. First correlation is usually originated from large specific volume of interfaces in nano-materials (up to 50%), and perfectness of crystalline lattice on the boundary. Structure of grain boundaries in nano-grained ceramics obtained under pressureless sintering and high-pressure sintering will be presented and the correlation of this structure with materials properties will be shown as well.

Size effect is a reaction of polycrystalline material on grain size decrease. Solubility variation in multicomponent systems, change of conductivity, electric and magnetic susceptibility are known in both nano-sized powders and nanograined solids. In the present paper there will be described in details the behavior of ferroics - the ceramics which is characterized by ferroelasticity such as ferroelectrics, ferromagnetics and stabilized zirconia-type of materials, where elastic energy relaxes inside the grains by twinning and domain structure formation.

# THE NANOCRYSTALLINE COMPOSITE Cu/W

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Tungsten and copper are immiscible elements. Interactions between the similar atoms  $F_{Cu-Cu}$  and  $F_{W-W}$  are stronger those for different ones  $F_{Cu-W}$ . Therefore, the atomic segregation are observed while the copper-tungsten melt is stirred. This segregation results in melt stratification. We prepared experimentally W-Cu alloys by mechanical alloying and by vacuum sputtering. It has been found that:

1. Cu-particles are enriched by tungsten impurities and W-particles — by copper ones at high energy mechanical alloying of powder mixture in a ball mill. However, this process is being slowed down as powder particles are ground up to nanometric size. The particles are beginning to move in the powder mixture as macromolecules (like Brown particles in a liquid) due to thermal fluctuations. As powder mixture temperature rise, the mobility of particles becomes more intensive. As a result of chaotic motion the particles segregate again: copper with copper and tungsten with tungsten. Thus, the nanocrystalline composites being formed because of Cu-Cu and W-W adhesion bonds are stronger then those between Cu and W. The interaction between W and Cu-nanoparticles is like W-Cu interatomic interaction.

**Conclusion 1:** It is very difficult to prepare homogeneous W-Cu alloy by the mechanical alloying.

2. W-Cu alloy we also obtained by coevaporation of tungsten and copper from separated sources and simultaneous deposition on a substrate. It was found, that vacuum sputtering results in particle segregation and nanocrystalline composite is formed too. The average grain size decreases when temperature of the substrate and partial vapor pressure reduces. As content of Cu is being reduced the Cu-nanoparticles average grain size decreases and W-nanoparticles grain size increases.

**Conclusion 2.** It is very difficult to prepare homogeneous alloys (Cu+50%at.W) by vacuum condensation of tungsten and copper vapor flows on substrate.

So-called pseudoalloy (by melting) or nanocrystalline composite material (by sputtering or by mechanical alloying) have been formed in all cases mentioned above.

# THE MECHANISM OF MET-CAR AND Cl-CONTAINING OR $\pi$ -BONDED MOLECULES INTERACTION.

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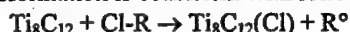
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Today binary molecular clusters  $M_8C_{12}$  ( $M$  = transition metal) so called "met-cars" are the subject of scientist's steady attention. These objects are novel unstudied structures, characterized with high stability, and those possess interesting phys.-chemical properties. In this job we study reaction ability of "classic" met-car  $Ti_8C_{12}$  on the basis of quantum-chemical calculations.

Cluster spin-polarized discrete variational method was used for our purposes.

The associations of  $Ti_8C_{12}$  with two kinds of molecules was considered: halogen-containing ( $Cl_2$ ,  $CHCl_3$ ) and  $\pi$ -bonded ( $CH_3CN$ ) molecules, those existence have been found with mass-spectrometer investigations [1]. The results of performed calculations are total and partial density of states, the values of overlap populations between origin atomic states, and electron charge distribution in cluster.

We may conclude that interaction between met-car and molecule, following with electron charge transfer from  $Ti_8C_{12}$  to halogen-containing molecule ( $Cl-R$  is typical case of such kind of molecules), lead to considerable decreasing of  $Cl-R$  atomic function's overlap population value and this is the reason of such molecule dissociation. This transformation is consistent with following expression:



In other hand, association  $Ti_8C_{12}$  and  $\pi$ -bonded molecules due to  $d(Ti) - \pi$  - bonding don't lead to significant redistribution of electron charge density in such complexes and molecules remain unchanged.

Obtained data verifies our assumption about the mechanism of associated molecule stability. We believe this is charge-fluctuation mechanism [2], essence of those is local deformation of basic electron term in associated molecule due to charge transformation..

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**INFLUENCE of the HEREDITARY FACTORS and COMPACTION  
METHOD of NANOPOWDERS ON STRUCTURE and  
PROPERTIES of CERAMICS on a BASIS  $\text{Al}_2\text{O}_3$ .**

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In this work analysed is an way leading from a method of obtaining initial nanopowders  $\text{Al}_2\text{O}_3$  with different dispersivity (14-250 nm), specific surface (6-120  $\text{m}^2/\text{g}$ ), degree of agglomeration, different range of particle sizes, to the choice of a compaction technique, modes of thermal processing and study of functional oxide ceramics properties. The plasmochemical powder  $\text{Al}_2\text{O}_3$  as the most agglomerated and possessing the widest range of grain size distribution revealed the worst compactibility. When the static pressure changes from 50 MPa to 500 MPa the relative density of samples made of such powder with binder did not exceed 55%. For the samples made of powders produced by hydrolysis and electrical explosion of the wire the relative density of samples with binder after the static compression composed 70%. The explosion compaction of the a.m. powders without preliminary granulation and use of binder enables to obtain relative densities ~ 83-88 % that is 15-20% higher as compared to the statically compacted samples with binder. It is conditioned by intensive processes of fragile destruction of particle sinters and other structural elements, their mutual friction and high temperature heating.

Studied are the laws of samples sintering in the temperature interval from 1350 to 1600°C, investigated is its influence on the crystallite size, porosity and their size distribution. The most dense preforms produced by explosion gave the more dense ceramics after sintering at 1400 -1500°C during 2 hours ( $\rho_{\text{rel}} \sim 98,0-99,5$  %). The increase of the sintering temperature from 1350 to 1550°C caused the growth of ceramics grain size from 100 to 500 nm. The samples made of powders produced by hydrolysis and electric explosion possessed the highest microhardness and fracture toughness ( $H_v \sim 17$  GPa,  $K_{IC} \sim 4,7$   $\text{MPa}\cdot\text{m}^{1/2}$ ).  $H_v$  and  $K_{IC}$  were 1,2 - 1,4 times higher for all samples compressed by explosion that was connected to the higher porosity and worse grain boundary connectivity in case of conventional static method. Rather high values of the compression strength ( $\sigma_c \sim 502$  MPa), bending strength ( $\sigma_b \sim 237$  MPa) and electrical strength ( $E \sim 18,8$  kV/mm) were obtained for statically compressed and sintered samples ( $\rho_{\text{rel}} \sim 88-93$  %) that was conditioned by a fine crystal structure.

# **SOL-GEL NANOCOMPOSITES WITH ULTRAFINE COPPER SULFIDE AND SELENIDE PARTICLES**

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A combination of required properties of optically inert matrices and active components is important under development of new materials with special optical features (absorption in a given spectral range, induced variation of the absorption under pulsed laser irradiation, photochemical effects). Optical materials by the type of semiconductor particles in glass matrices are of undoubted interest in this respect. They were manufactured both in the form of monolith and thin films on different substrates. Most of similar materials, including those produced in industry, are a silicate matrix with small particles of sulfides and selenides of Cd, Zn, Pb. In the present communication we collect the results of studies concerning materials on the basis of silica matrices with incorporated nanosized particles of copper compounds (various phases of sulfides and selenides) with a series of features in linear and nonlinear optical properties.

Usage of the sol-gel technique for production of nanocomposite materials allows to control the nature and concentration of doping elements and to carry out a sequence of solid state chemical transformations. The main steps of the processing are the following: sol preparation, gelation, drying, and annealing in the controlled atmosphere. They resulted in matrices with uniformly distributed ultrafine  $\text{Cu}_x\text{S}$  and  $\text{Cu}_x\text{Se}$  particles. The composition materials were characterised by XRD, XPS, TEM, RBS. Their optical features are associated both with quantum confinement effects and chemical modification.

The sol-gel technique of fabrication of similar complex nanocomposites with given optical and mechanical properties opens new pathways for creation of perspective optoelectronic devices.

## MONOFIBRES SiC WITH NANOCRYSTAL COATING OF Ti-Al

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The object of research is the sintering of nanocrystal coating of Ti-Al (Al(4-5at%)) on SiC fibers using a method of internal friction. 100 microns thick coating was formed on fibers (diameter 100-110 microns) by coating with suspension consisting of vacuum oil and nanocrystal Ti-Al. As the area of coating section exceeds the SiC fibers cross-section nearly in eight times, it's possible to consider that samples are the least element of a composite material of Ti-Al-SiC with the volumetric contents of fibers ~ 0,1. The suspension based on a nanocrystal powder was synthesized by simultaneous condensation of Ti-Al and vacuum oil vapours on the same substrate. During this process, there occurs not only the formation of nanoparticles, but also their conservation in the oil, that is important for nanoparticles of chemically active Ti. It is determined that evaporation of oil and stacking of nanoparticles in a dense monolith take place during heating of a coating up to 400-600 K in hydrogen at pressure 1-2 Pa. With the further heating there comes sintering. In initial state nanoparticles of Ti-Al have body-centred cubic structure. After sintering at  $573 \pm 10$  K, during 8 hours body-centred cubic structure is replaced by typical  $\alpha$ -modification of Ti structure. A temperature of sintering decreases with the reduction of a diameter of nanoparticles. The elastic modules of SiC fibers with a Ti-Al coating at first grow during sintering, and then this growth slows down, that illustrates the end of the second stage of sintering.

Conclusion: thus, the use of nanoparticles of Ti-Al allows to receive a dense coating on the SiC fibers.

# CRYSTALLOGRAPHY OF CONTACT LAYERS & SELF-ORGANIZATION PROCESSES UPON SYNTHESIS OF ULTRA DISPERSION SYSTEMS

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In technologies of synthesis of solid state materials there is a particular state of matter -a contact interface layer (CIL). Its properties are considerably different from those of the neighbour volumes. In many cases the processes in the CIL determine the final properties of product material, it especially concerns ultradispersive systems (UDS), such as composite multilayer materials, nanocrystals, fine powders, aerosols, gels etc. Crystal-line interfaces are the main defects of the UDS. The space symmetry of adjacent crystals and their mutual interconnection are a key to the structure and properties of interfaces, topology of interfacial defects, morphology of embedded crystals (precipitates), epitaxy and domain formation, 2D-3D phase transformations during film growth and other contact phenomena in the UDS. The substance in the CIL exists in nonstable state of bifurcation cascade. According to the S-theorem of entropy diminution in self-organization processes [1], the low energy interfaces may be considered as strange attractors for consolidation process of the UDS. If one assumes that the CIL is an information processor with stochastic entrance, then the appearance of new information on a level of physical realization corresponds to nuclei of new phases and cooperative correlations between them. This transition is metastable and its duration is determined by external parameters. Experimental contact phenomena, dissipative structure formation during consolidation of metal nanoparticles (Ni,Cu) and thin film growth (Ni/GaAs,Bi/SiO<sub>2</sub>, Si/Ge etc.) were discussed on a base of the symmetry theory of interfaces, the theory of self-organization and the system analysis [1-6]. The investigation of the CIL evolution is not only theoretical interest but it is necessary to create the effective technologies, based on synergetic resonance principle.

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**SEMINAR N.  
TESTING**

**335-350**

### NEW METHODS OF MICROMECHANICAL TESTING OF MATERIALS BY LOCAL LOADING WITH A RIGID INDENTER

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The method of determination of hardness and microhardness has been used for many years widely for evaluating the mechanical properties of materials in both scientific-research laboratories and in industry. However in recent years, the method of local loading of materials (LLM) with a rigid indenter is being transformed from the method of evaluating the mechanical properties into a method of determining a set of mechanical properties (yield stress, strength, ductility, Young's modulus, ductile-brittle transition temperature, fracture toughness, etc). On the one hand, this is caused by the development of completely new devices and, on other hand, by the development of the theory of indentation of materials. The development of the method of determination of the mechanical properties by LLM is of special interest for investigating brittle ceramic materials. This is due not only to the fact that the application of LLM makes it possible to avoid complicated processes of the preparation of ceramic specimens for mechanical tests but, more importantly, it is the appearance of completely new possibilities for determination of the mechanical properties of brittle materials. For example, only LLM makes it possible to determine the yield stress of these materials or compare the ductility of two ceramic materials that are destroyed in a brittle manner in mechanical tensile, compression and bend tests.

Only LLM can be used to examine the mechanical properties of thin coatings and separate phase components of composite materials, and also analyse the mechanical properties of different zones of welded joints and other structures with the properties changing through the cross section.

In the report new experimental procedures of micromechanical tests of materials by the LLM using a rigid indenter, are described. These procedures make it possible to construct  $\sigma$ - $\epsilon$  deformation curves, and determine the characteristics of strength and plasticity of materials, Young's modulus and strain hardening. In addition to the procedures described for the determination of fracture toughness, ductile-brittle transition temperature, anisotropy of mechanical properties, etc., LLM is the universal method for the investigation of mechanical properties.

## POSSIBILITIES OF ACOUSTIC METHODS TESTINGS OF POROUS MATERIALS

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The technology of creation of powder materials of special purpose represents a circuit of various processes and operations associated to formation of a certain internal structure of a material on each stage of manufacturing. A desirable outcome is deriving a material with the beforehand given properties. Therefore important problem of powder metallurgy is the possibility of monitoring of modifications of this structure in process and entire quality monitoring of production in an outcome of production. The effective tools of a solution of this problem can be acoustic methods of not desroying monitoring.

The concept of acoustic methods implies wide area of various methods and expedients based on use of elastic oscillations and elastic waves, and permitting to determine such physical - mechanical features of materials as an elasticity, not-elasyicity, fatigue, to control defects of a structure, quality of baking of a material. The effective using of acoustic methods in powder metallurgy requires the individual approach to a solution of each concrete problem and has singularities depending on properties of controlled object.

The methodology of application of acoustic methods for a solution of the indicated circle of problems of powder metallurgy considering the features of porous space of materials is developed. The instrument complex is created and the special methods permitting to do a measurements of acoustic features in materials with a various degree of a porosity are developed. The offered methodological principles are confirmed by a cycle of experimental researches.

Is shown, that diagnostics of a condition of powder materials during their manufacturing, monitoring of their quality and measurement of physical-mechanical performances on any stage of production can be made on measurements of acoustic parameters of elastic oscillations and elastic waves for a range of porosities from 0 up to 95%.

# INVESTIGATION OF OXIDE FERRO-, PIEZOELECTRIC CERAMICS AND CONTROL OF THEIR PROPERTIES BY RADIOSPECTROSCOPY METHODS

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Useful for applications in the devices of engineering electronics properties of piezoceramics on the base of  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  (PZT) are usually received by doping of PZT with impurities of different oxides such as  $\text{La}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{MnO}_2$ ,  $\text{CuO}$ ,  $\text{Cr}_2\text{O}_3$  and others. Control of these impurities and their influence on the properties of piezoceramics is one of the main problems of the improvement of quality and creation of new materials for engineering electronics.

ESR spectra measurements of manganese and iron ions in PZT ceramics with  $\text{Nb}_2\text{O}_5$  or  $\text{La}_2\text{O}_3$  impurities (from 0 to 10 %) are provided. It was found that manganese charge states changes as  $\text{Mn}^{4+} \rightarrow \text{Mn}^{3+} \rightarrow \text{Mn}^{2+}$  with the increasing of La or Nb concentration.

The NMR and ESR spectra were measured in PLZT (8/65/35) with Cr, Ca and Cu also. The observed NMR spectra peculiarities were shown to be dependdnt on lanthanum and copper content and connected with a distribution of chemical shift tensor values and their principal axis direction. ESR spectra were shown to be those  $\text{Cr}^{3+}$ ,  $\text{Cr}^{5+}$ ,  $\text{Ca}^{2+}$  and  $\text{Ti}^{3+}$  their intensities being dependent on the La content.

The investigation of  $^{93}\text{Nb}$ ,  $^{45}\text{Sc}$  and  $^{207}\text{Pb}$  NMR spectra in PMN, PSN and mixed  $(\text{PMN})_x(\text{PSN})_{1-x}$  relaxor ferroelectrics have been carried out. The temperature dependence of line width and spin-lattice relaxation time are shown to be connected with Nb ions motion in PMN. The Nb ions shift into [111] type directions and their thermal reorientation between these directions were described by the Vogel-Fulcher law. The displacement of Sc ions along [001] type directions in the regions with random distribution of Sc and Nb is found from  $^{45}\text{Sc}$  NMR spectra peculiarities. In solid solution  $(\text{PMN})_x(\text{PSN})_{1-x}$  the regions around Sc ions are shown to be ordered at  $x \geq 0.5$ . The mechanism of this ordering is discussed in the framework of random fields model.

## NEW METHODS AND CRITERIONS OF AN EVALUATION TRIBOTECHNICAL PROPERTIES OF MATERIALS

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Studies have manifested that in case of deformation in sliding friction a variety of metals and alloys have similar relationships of electron work function of a rubbing friction to normal load with three typical portions in dry and boundary friction. Portion I demonstrates the work function with increase in load. It declines on the rubbing surface in portion II and remains unchanged in portion III, irrespective of load rise, or it increase insignificantly. In case of seizure the friction torque and volume temperature rise sharply, while the work function does exactly the contrary. The given dependence is observed in a broad band of velocities.

The long-term tests for want of loads appropriate to portion I and II, have not registered destruction of a surface layer of materials, and for want of similar tests in III portion were observed emerging spots of destruction on a surface.

The studies have manifested that the load of transition from a portion II to a portion III may be an objective criterion of an rating the applicability of materials in friction units. Comparison of such rating with full-scale tests has demonstrated that criterion yields a more objective evaluation, than bench wear tests.

# TESTING LAYERED CARBON COMPOSITES BY EDDY CURRENT METHOD

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The constructional composite materials on the basis of carbon composite fabric have unique mechanical and thermal physic properties at small density. The testing of a composite material by non-destroying methods allows to judge the conformity of the actual characteristics to calculated ones, to reveal breaking and other defects. Periodicity of the material structure created by level-by-level laying of reinforcing fabric into the matrix of a binding substance stipulates a strong anisotropy of properties in longitudinal and transversal extension of layers directions. A number of strength and other essential characteristics is determined by volumetric content of reinforcement, thickness values of alternating layers and their properties.

Comparatively weak specific electrical conductivity of carbon composites of  $\sigma < 10^5$  predetermines testing on frequencies 20-100 MHz by eddy current converters (ECC) that are included in a high-quality resonant system. Structure-scopy from the side of a surface which is parallel to the boundaries of layers is complicated by shielding effect of a higher layer; more favorable opportunities for determining the integral characteristics of the composite and parameters of separate layers are offered when scanning the surface in relation to which the layers are arranged vertically. On the basis of research of rectangular ECC field distribution in the composite material when ECC is situated along and across the layers, the formulas for calculation of corresponding conductivity of a material are obtained:

$$\sigma'' = \left[ \frac{P_{\Sigma}}{2\Theta l a^{\tau} (\omega \mu_0)^{\tau/2}} \right]^{\frac{2}{\tau-2}}; \quad \sigma' = \left[ \frac{T_1}{T_1 + T_2} \sigma_1^{-\frac{\tau+2}{2}} + \frac{T_2}{T_1 + T_2} \sigma_2^{-\frac{\tau+2}{2}} \right]^{-\frac{2}{2+\tau}},$$

where  $T_1, T_2, \sigma_1, \sigma_2$  – thickness and conductivity of the reinforcement and binding element layers;  $P_{\Sigma}$  – dispersed-in-layers power;  $\ell$  and  $a$  – length and width of (ECC);  $\omega$  – circular frequency;  $\mu_0$  – magnetic constant;  $\Theta, \tau$  – constants for a certain range of the parameter  $\beta = a\sqrt{\sigma\omega\mu_0}$ .

Inverse problem of testing (determining of  $T_1, T_2, \sigma_1, \sigma_2$ ) is solved on the basis of the drive characteristics  $\sigma''$  received at ECC moving across the layer.

**EFFECT OF THE SMALL PERITECTIC TEMPERATURE  
OVERSTEPPING AND COMPRESSION POWER DURING HTS-  
CERAMICS SYNTHESIS ON RADIO-FREQUENCY ABSORPTION  
CHARACTERISTICS**

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Possibilities of using the superconducting ceramics are sharply limited by their critical current density which, in turn, depends on the quality of both granules and intergranular contacts. There are variety of technological approaches improving these characteristics. Changes of temperature and pressure in the process of ceramic synthesis including the peritectic temperature overstepping belong to such approaches.

The method of radiofrequency (rf) losses measurement upon applied dc magnetic field was suggested to check the changing quality of intergranular medium and granules. The steepness of increasing rf-energy absorption under initial entering the magnetic field can characterize a quality of contacts between granules, while the relative values of losses at the minima in the decreasing magnetic field and in the trapped one are the criterions of granules quality. It has been shown that increase of fabrication pressure (up to 8 tons/cm<sup>2</sup>) results the reducing steepness of absorption growing under initial elevating of magnetic field that witnesses about improving intergranular contacts. This process is the most brightly manifested itself at high temperature pressing. It is also observed the reduction of losses at the minima of the magnetic field dependencies that indicates improvement of granules characteristics. Short time heating above the temperature of peritectic in the process of synthesis rises a value of critical current and simultaneously reduces sharply both a rate of growing of losses when the magnetic field grows and absorption at the minima of the magnetic field dependences.

Thus our method of analysis of magnetic field dependences of the rf absorption allows to differentiate the mechanisms of the magnetic field influence on intergranular medium and granules as well as to realize an undestructive monitoring of characteristics of ceramic samples obtained by means of varying the technological approaches of synthesis.

## INVESTIGATION OF MECHANICAL PROPERTIES OF $YB_{66}$ BY INDENTATION TECHNIQUE

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Yttrium polyboride  $YB_{66}$  has a very complicated crystalline lattice. The elementary cubic cell of this lattice with the lattice constant 2.344 nm consists of 8 supericosahedral configurations of 156 atoms each, and each supericosahedron is a cluster of 13 icosahedra  $B_{12}$  which form a pentagonal pyramid. Y atoms occupy 50% of voids between supericosahedra.

Mechanical properties of  $YB_{66}$  are practically not studied: in the literature there are the data of two works for measuring hardness which are not in agreement to one another. The investigation of  $YB_{66}$  mechanical properties is of great scientific interest for the characterization of properties level and deformation mechanism in a material with so complicated lattice. In particular, it is interesting to check the availability of similarities in the behaviour while deformation of polyborides and quasicrystals which also have a pentagonal symmetry in atomic stacking, but, as distinct from polyborides, in the absence of translational symmetry. A similarity in the behaviour of electronic properties of higher yttrium borides and quasicrystals already established.

A great practical interest to mechanical properties of  $YB_{66}$  is stipulated by its application as a soft X-ray monochromator for synchrotron radiation.

In the presented work there was first used for studying  $YB_{66}$  polycrystal a unique procedure for obtaining the deformation curve with using a set of trihedral diamond indenters with various angles at the tip. In addition, there were carried out studying the dependence of hardness on the magnitude of the load at room temperature, measuring hardness at 78 K, and the evaluation of the elasticity modulus by the technique of microindentation with the record of loading diagram as well. Indentation prints were studied in scanning electron microscope.

The behaviour of  $YB_{66}$  while indentation is discussed in comparison with the behaviour of a quasicrystalline polycrystal  $Al_{63}Cu_{25}Fe_{12}$  as well as of a wide variety of crystalline materials (metals, nitrides, carbides, semiconductors, diamond).



### MOISTURE TRANSFER IN A NEW ALUMINUM GLASS FIBER REINFORCED PLASTICS LAMINATES

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New metal-polymer composite laminate materials (SIAL) are worked out in VIAM (abroad analogs are ARALL, GLARE Laminates). SIALs are having the advantages on strength, small cyclic fatigue and crack protection in comparison with aluminum alloys.

The properties of moisture transfer in new tested materials are investigated. The sorption measurements, modeling the hard climatic conditions (temperature is 60 degrees centigrade, relative humidity is 100%), are carried out. The samples with various sized along and cross to the primary direction of the reinforcement of glass fiber reinforced plastics (GFRP) was prepared (structure of reinforcement are 100:1 and 70:30). Any damages on surfaces of samples have been absent during more then 100 days of moistening. After 20 days of moistening it is seen decrease of samples' moisture content, especially on narrow samples with a cross direction to the primary direction of the reinforcement. This decrease is caused by chemical reaction in GFRP, which was seen early on separate exposed GFRP. The relaxation time is compared with time of diffusion, therefore, SIAL samples, sorpting moisture from edges, are not submitted to Fick's law of diffusion. Moisture is an active plasticizer of GFRP, due to matrix partial glass transfers, which causes the change of stress field in matrix. According to dynamic mechanical analysis the glass transition temperature decreases after moistening from 120 to 70 degrees centigrade, but after drying restores to 110 degrees. Moisture is a catalyst of micro-damage development. After 150 days of moistening aluminum layers have been corroded that is a cause of increase of samples' sorption capacity. After 170 days of moistening aluminum have been partial broken from surface.

The diffusion model considering nonfickian behavior of diffusion; material's properties anisotropy; dependence of diffusive coefficient by sample size; damage after cutting edge; effective chemical reaction in samples is proposed.

PRESENTATION OF POROUS SPACE  
IN ACOUSTIC FIELDS OF LINEARLY - ELASTIC MATERIALS

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The porous materials find wide application in various industries. The shaping of properties of these materials in many respects is connected with creation of the certain structure of porous space. Therefore the studying of features of porous space plays the important role and for improvement of technology of creation of a material, and for control of its quality. Perspective for a solution of these problems the acoustic methods of not destroying control are.

The application of acoustic methods for a research of a structure and monitoring of defects of porous materials assumes knowledge of regularities of shaping in them of acoustic fields as functions of parameters of a structure, in particular of features of porous space, and correlation between parameters of an elastic wave and porous space.

The analysis of structural singularities of various kinds of porous materials has shown, that, depending of structure of porous space, history of its creation, wave sizes of pores, kind and level of a loading, connection of parameters of a structure of these materials and an elastic wave should describe within the framework of various acoustic models of a material.

So, in case of small levels of a loading, being characteristic for not destroying methods of researches, the good baked a porous material it is possible to consider as linearly - elastic medium with losses stipulated mainly by scattering. For this model within the framework of a mechanics of continuous mediums, i.e. in case of rather small porosity, the condition of a material, including of porous space can be circumscribed appropriate to a degree of an anisotropy by an amount of complex modules of an elasticity (for an isotropic skew field - two) and by it's denseness. And also the valid part of modules of an elasticity is stipulated by only elastic properties of a material, and imaginary - it's not elasticity. Acoustic reflections of these features of a material bearing in a state information of porous space, are for the valid parts of modules of an elasticity - the velocities of propagation, and for imaginary - damping factors of appropriate types of elastic waves.

Thus for featuring of porous space it's enough to know the pointed parameters of elastic waves .

**APPLYING OF THE INDENTATION METHOD TO STUDYING  
MECHANICAL PROPERTIES OF QUASICRYSTALS OF THE  
SYSTEM Al-Cu-Fe**

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Quasicrystalline materials are the objects in which packing of atoms is described by a rotation axis of 5- or 10-fold symmetry. A feature of such packing is the absence of translational periodicity. In quasicrystalline materials there exists the periodicity of long-range order (over distances significantly in excess of interatomic ones). The special stacking of atoms in quasicrystals causes the special character of their mechanical properties. In particular, at macroscopic strain at ambient temperature quasicrystals are brittle materials with practically zero plasticity.

In the report the results of the examination of mechanical properties of quasicrystalline material  $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$  by a method of indentation are presented. The applying of a new method for determination of mechanical properties of low-plasticity materials with usage of a set of trihedral diamond indenters with different angles at the tip for the first time has allowed to obtain a stress-strain curve at ambient temperature similar to the stress-strain curve obtained at uniaxial loading. It is shown that as opposed to crystalline materials there is observed not hardening, but sharp softening during deformation.

For the first time for this material the temperature dependence of hardness in the temperature range 78-1073 K was obtained. At temperatures lower than 673 K there is detected an athermic section distinctive for semiconductors (Si and Ge). As well as in semiconductors, such effect apparently, is a consequence of a phase transition to more ductile phase aroused by high hydrostatic pressure under the indenter, or sharp softening during deformation. Plasticization of a material under the indenter is confirmed by the formation of "tongues" (thin layers squeezed out from under the indenter) around of the indentation print.

# QUICK-FORECAST OF AN ELEMENTS COMPOSITION AND OPTIMIZATION OF A COMPONENT RELATIONS FOR A EW MATERIALS ON A BASIS OF 3d-METALS

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The Combined Approach from [1-5] are discuss. It's preposed to make by means of  $\Delta N/N$ , % of an atomic /molecular characteristics quick-forecasting of on principle of the elements composition and a quality estimations of fluctuations due to an small impurity atoms. To appreciate the physical -chemical role a second elements in forming different effects, or to make conclusions about the properties level of binary alloys, one must have some the (derivative from  $\Delta N/N$ , %) auxiliary microscopical parameters' ( $\pm PEV$ ,  $\pm PEICh$ ,  $\pm VMP$ ,  $\pm PIEMR$ ). The Athors elaborated three types of the Certification s Card (CCI, CCII, [1]; CCIII [5]) and tables. The CCI - is the Certification Card "One a soluble element-multitude a changeable solvents"; CCII - is "Multitude a soluble elements-one a constant solvent"; CCIII - settles correlations between enthalpy of equiatomic alloys formation, solubility of chemical second Elements in a solid-state of 3d-metals - solvents;  $\Delta N/N$ , % elastic modulus, other properties and parameters PEV, VMP, etc.

Optimization of the component relations was made by means of quantum-mechanical calculations of a concentration dependences (across 1-2 at %) for the energy band parameters of binary alloys "3d-metal-second elements". The verifyng of method has been made on alloys: Ti-M(M-Sc, V, Cr, Fe, etc.), Cr-M(M-Ti, V, Fe, etc.).

Parameters: PEV- mutual energy influens of components; PEICh - electrochemical activity for components of binary system; PIEMR - change of energy states of elementary volume; VMP - auxiliary microscopical parameter of the enthalpy change of elementary volume of binary system.

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### THE ACOUSTIC CHARACTERISTICS OF THE ANTIFRICTION POWDER MATERIALS ON THE BASIS OF IRON

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The wear resistance of low cost sintered powder materials on the basis of iron, in some times exceeds the wear resistance of bronze, brass, babbitt. Despite of it, in many laboratories of the world the works on perfection of these materials proceed.

In the given work the attempt is made to establish correlation of the acoustic characteristics - speed of a sound and factor of attenuation - with parameters of structure and technology of reception of a number of materials on the basis of iron powder.

Samples for researches were made from an iron powder IDKP3.200.26 (ГОСТ 9849-86) with various porosity from 2 up to 20% and additives of the copper powder ПМС-1 (ГОСТ 4960-75), graphite ГК-3 (ГОСТ 17022-81), bronze ПЭК 03.200.8 (БрОЦС-4-4-4),  $\text{CaF}_2$  (ГОСТ 7167-77). Samples pressed at room temperature, and then sintered at 1050°-1150°C in an atmosphere of ammonia dissociated within 1-2 hours. The part of samples was made by a method of dynamic hot pressing at temperature 1100°C within 10 minutes. Some were samples subjected to a number of modes of heat treatment including annealing, tempering and hardening.

The researches were carried out on an acoustic instrument complex IMS NASU at the frequencies of 0,6 and 5 MHz.

The heat treatment is established, that: the annealing and the tempering raises, and hardening reduces factor of attenuation of a material.

It is shown, that a material with heterogeneous structure [a matrix + the soft inclusions (graphite, copper etc.)] have higher modules of elasticity, factor of attenuation and module of losses, and with reduction of porosity and, is especial for materials received by a method of dynamic hot pressing, the influence of presence in structure of a material of the mentioned inclusions raises.

The increase of temperature of sintering with 1050 up to 1150°C does not render appreciable influence on the dampening of the characteristic of materials.

### EFFECT OF POROUS SILICON COMPOSITION ON ITS PHOTOLUMINESCENCE

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Correlation between the composition and the photoluminescent properties of anodically formed porous silicon (PS) films produced by additional treatment in 48% aqueous HF as well as further ageing in the air was investigated.

The treatment of samples in hydrofluoric acid is established to result in a change of photoluminescence intensity (PLI) and sometimes in a shift of PL peak. When storing the samples both as-prepared and etched in HF, a rise of PL intensity was observed. The PLI value of HF-treated sample flattened out within about a month, whereas that of the untreated one reached the maximum within approximately a year.

The data of secondary ion mass spectroscopy and Auger spectroscopy have demonstrated that the PLI rise during ageing is accompanied by an increase of oxygen content in PS. IR transmission spectra have shown no bonds except Si-Si and Si-H<sub>x</sub> ones in the PS samples as-treated in hydrofluoric acid. As a result of a week's ageing of such samples in the air, the absorption bands attributed to Si-H<sub>x</sub> bonds have disappeared from IR transmission spectra, whereas those associated with bonds in Si-O, Si-OH, O<sub>2</sub>-Si-H complexes have appeared. Subsequently, only amplification of Si-O bands was observed. Similar changes with much smaller rate occur in the samples untreated in HF.

The described results are analyzed within the sensitized photoluminescence model in which the absorption of the excitation quantum is suggested to occur in the oxide film at the surface of silicon nanostructure, while the radiative recombination is supposed to take place in Si nanocrystallites.

## SUBATOMIC-SCALE FIELD ION MICROSCOPY OF GRAIN BOUNDARIES

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The first atomic-level observations of grain boundaries (GBs) by the method of field-ion microscopy (FIM) made a valuable contribution to the progress in understanding atomic structure of the intergranular boundaries. But the definition of the fine-scale atomic structure of the GB core is below the routine resolution of a FIM. In this work the method of indirect magnification is used in FIM investigations of the atomic structure of GBs. The method offers a further degree of FIM resolution. The calibration of individual atom displacements against the known deformation field of the single lattice dislocation showed that the method allowed to detect a subatomic local displacement in the vicinity of line and planar defects of order of 0.01 nm. A computer simulation of symmetrical GBs was also produced. The technique used in the computer experiments was the pair-wise version of the molecular dynamics method.

The data provided by the subatomic-level FIM combined with real-space computer simulation showed that in addition to the rigid-body translations of lattices at symmetric grain boundaries observed in tungsten crystals, there also exist zonal displacements of atomic planes. In the present paper the applicability of analytical model of high-angle GBs to description of the relaxation due to rigid-body translations of lattices of the adjacent grains and zonal plane displacements was investigated. Analyzing the atomic morphology of symmetric boundaries in different translation states showed no changes of geometry of atomic layers in GB cores. It is established that the atomic configuration of the cores of symmetric grain boundaries can be adequately described by using a limited numbers of parameters, which characterize the translation state of boundary-core planes. These allows for a rigorous analytical analysis of symmetrical GBs in a commensurate case. It was shown that taking into account of the rigid plane translations allowed to obtain analytically the same atomic configurations as in case of detailed molecular dynamics solution. Subatomic displacements at an incommensurate GBs are determined by the FIM methods and analyzed in terms of the reciprocal-space analytical model.

### Semiconductor-based gas sensitive substances for methane analysis in air

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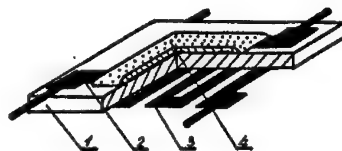
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At present semiconductor sensors are becoming more and more popular means of environmental analysis. The sensors' gas sensitive substances are based on metal oxides. The sensors feature small size and mass, high sensitivity and response, ability to operate in a wide range of ambient temperature. The sensor's operation principle is its electrical resistance variation under exposure to detected gas.

Though such semiconductor sensors feature high sensitivity of a number of gases, it's impossible to determine small concentrations of methane. The main reason for this, is low reactivity of the latter. In the IAPPB a gas sensitive substance capable of detecting methane on 10 ppm level has been synthesized (fig.1). The substance is based on tin oxide doped by antimony. The compound was also modified by palladium in different concentrations which, according to the general mechanism of the sensor operation [1], increases the sensor sensitivity of methane. It's been experimentally proven that palladium in the optimal concentration increases the sensitivity dramatically. The work also presents explanation of the observed effects on the basis of the mechanism of heterogeneous catalytic reactions running at the sensitive substance's surface.

Fig.1 . Sensor design  
1-ceramic base, 2 - measuring electrodes, 3 - heater, 4 - gas sensitive layer



The obtained results can be applied for creating devices purposed for analysis of methane exhausts into environment.

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**NEW RADIOPROTECTOR "NECTAR" USED FOR  
TREATMENT OF THYROID GLAND EXPOSED TO  
RADIONUCLIDE  $^{137}\text{Cs}$  EFFECT**

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Thyroid gland disease rate including cancerogenic ones, for children that live in regions rich in radionuclide  $^{137}\text{Cs}$ , has been increasing the last years, due to the Chernobyl disaster which led to a weakening of hormone activity of thyroid gland {1}.

The rate of thyroid gland disease has been found to grow due to an accumulation of radioactive cesium in human body as a result of a short period of half-decay of iodine ions and high affinity of  $\text{Cs}^+$  to  $\text{I}^-$  ions attributed to a peculiarity of the electron structures of these elements, of interaction activity with formation of stable electronic states in cesium atoms due to an easy transfer s-electron having a weak bond to its nucleus, and formation of stable  $s2p6$ -configurations in iodine atoms {2}.

Ions  $\text{Cs}^+$  form complex compounds comprising  $\text{CsI}$  with their hormonal activities disturbed, as a result of a donor-acceptor interaction of the thyroid gland hormones TTG,  $\text{T}_4$ ,  $\text{T}_3$ , etc) with the iodine ions.

A new non-toxic, specific radioprotector "NECTAR" that provides an active elimination of cesium ions out of the human body, restoration of bio-chemical and patho-morphological changes, reduction of radioactivity, has been developed based on theoretical and experimental researches, which is recommended for the use as curative and/or preventive mean at thyroidal pathology.

**SEMINAR O.**  
**INDUSTRIAL APPLICATION**

**352-366**

HIGH-SERVICE-LIFE WELDING TOOL FROM DISPERSION  
STRENGTHENED COPPER OF THE DISCOM® TRADE MARK:  
EXPERIENCE OF PRODUCTION, ADOPTION AND  
INTERNATIONAL DELIVERS

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One of the fields of high-effective application Oxide and Carbide strengthened copper (OCDS-Copper) of the DISCOM® trade mark developed by the Scientific and Technological Firm TECHMA is welding production. These materials are successfully employed for manufacturing of contact tips for MIG/MAG-welding, spot welding electrodes, plasma torches nozzles, soldering irons tips and others.

Steadily increasing application of welding tool made of the mentioned materials is caused by considerably longer service-life (2...5 times) of this welding tool in comparison with service-life of welding tool made of traditional electrotechnical sorts of Bronze (CuCr, CuCrZr, CuNiTiBe and others) at the same prices.

Peculiarity of these articles is that in most cases it is necessary mechanical processing for their fabrication. Here we consider mechanical treatment of not usual traditional sorts of Bronze but mechanical treatment of materials having fibrous structure and high hardness ( $HV_{30} = 1700...2800$  MPa). Besides, especially according to requirements of foreign customers, the articles must have very close tolerances of sizes, high surface quality and aesthetic appearance (absence of any marks, spots and etc.).

Thanks to the techniques of mechanical process developed by the Scientific and Technological Firm TECHMA and special lubricating and cooling fluids of the TECHMOL® trade mark all the problems connected with process of OCDS-Copper of the DISCOM® trade mark have been managed to solve.

It has offered to fabricate industrially high-life service welding tool from OCDS-Copper of more than 100 types and sizes in both Scientific and Technological Firm TECHMA and JSC CHEBOKSARY AUTOMOBILE AND AUTOMOBILE REPAIR WORKS.

Main consumers of this tool besides 200 works of Russia are also a number of firms of the USA, Germany, Austria, Southern Korea, Sweden and other countries.

### **EXPERIENCE OF MANUFACTURING PARABOLIC MIRRORS - CONCENTRATORS OF A SOLAR ENERGY FROM COMPOSITE MATERIALS**

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With the purpose of creation of the solar power installation working in space environments was developed and realized the process of manufacturing of a parabolic mirror - concentrator of diameter 9 meters consisting from 36 separate sectors.

Designer and technological study have allowed to receive necessary accuracy of geometry of a construction using as base of a sector structure sandwich panel consist of graphite skin and aluminium honeycomb core. For creation of mirror coating the process engineering of deposition on graphite skins of a reflecting sublayer from an epoxy compound was developed. To obtain a mirror surface on the sublayer was applied a vapor deposited aluminium layer and protective coating.

During development and manufacturing of a sector of a mirror - concentrator the problems vacuum curing of a double curvature sandwich were solved, the sizes of sheets are determined in view of minimum permanent stresses in a construction, the technological methods shearing of graphite skin with a mirror layer and deposition on them of protective technological coating are completed.

The technology process of manufacturing includes the following operations: forming flat graphite skin; deposition of a reflecting sublayer and mirror coating; shearing sheets and honeycomb; staged vacuum curing sandwich on a technological equipment; curing quality control; the geometry control of a construction and quality of mirror coating.

Experimentally is confirmed, that the developed technology allows to realize necessary accuracy of geometry construction, and the selection as a skin graphite sheets with low coefficient of thermal expansion provides necessary geometry stability in an effective range of temperatures.

The main technological problems requiring of further studies and researches are connected to increase of quality and improving of a reflecting sublayer properties in range of temperatures from - 50 up to + 100 C.

### DEVELOPMENT AND RESEARCH SOLAR ENERGY PARABOLIC MIRROR-CONCENTRATOR CONSTRUCTION FROM COMPOSITE MATERIALS

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One of the perspective directions of development of new class power increased (more than 10 KW) electric stations working in space environments are use of solar radiation energy by means of concentration and consequent transformation with the help of closed gas generator cycle in electrical energy.

With the purpose of implementation of the given project was developed and made parabolic mirror-concentrator construction of 9 meters diameter in a uncovered condition.

The mirror - concentrator represents itself a transform construction consisting of 36 separate sectors. The sectors is a sandwich structure panel with a specific double curvature geometry and stiffening beam. The sandwich structure consist of face and back grafite skin bonded to the core with a curing adhesive. The face skin surface has a reflecting sublayer from polymer and mirror coating with mirror reflection not lower 0.85, solar absorptance factor less 0.18, the degree of blackness is not lower 0.35.

During development the behaviour of the construction and functionability of reflecting coating in range of temperatures from - 50 up to + 100 °C is investigated. The realization complex thermo vacuum tests imitating full-scale effect, implemented both on separate samples, and on full-scale sectors of a mirror - concentrator with watching of change of a focal length and dispersion of a light spot.

Influence of speed of heating of mirror coating to value of a mirror reflection factor experimentally is established.

By research results the inference about conformity to the basic technical requirements and mirror coating characteristics is made.

The main problems requiring of the further analysis and study are connected to adaptation of a reflecting sublayer structure and increase of its resource of activity without essential degradation of mirror properties, and also increase dimension stable of the construction at thermo cycles.

PRODUCTION TECHNOLOGICAL ASPECTS OF SIZED BARS  
FROM OXIDE AND CARBIDE DISPERSION STRENGTHENED  
COPPER OF THE DISCOM® TRADE MARK

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Oxide and Carbide Dispersion Strengthened Copper (OCDS-Copper) of the DISCOM® trade mark developed by Scientific and Technological Firm TECHMA has been widely used in different branches of industry lately. They are delivered to customers mostly as ready-made articles manufactured preferably from hot moulded semi-finished items (bars, tubes and other shapes). Here a considerable part of the material is wasted in the form of chips.

The present technology of getting sized semi-finished items from OCDS-Copper by means of centreless grinding with subsequent drawing provides significant wasting reduction at mechanical process, but sized in this way semi-finished items are more expensive than hot-moulded ones.

As a result of carried out research the technology of getting sized semi-finished and cheaper items made of OCDS-Copper has been developed. This technology is based on heat process of powdered briquettes before hot extrusion in special reusable capsules; extrusion without elements cladding the surface of the semi-finished item; subsequent finishing operations ensuring semi-finished items size according to h11 and high surface quality.

Bringing this technology to a commercial level offers to reduce critically expenses on initial powder copper and alloying elements and to reduce accordingly the cost of the semi-finished items. But first of all this technology makes possible to produce semi-finished items made of OCDS-Copper not only for Russian market but also for foreign customers.

Manufacturing of sized semi-finished items is carried out by Scientific and Production Enterprise KERMET.

**POTENTIAL CARBON/CARBON COMPOSITES FOR  
FRICTIONAL SYSTEMS OF AIRCRAFT AND AUTOMOBILE  
APPLICATION**

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A range of researches has been conducted aimed at the development of promising carbon/carbon composites for frictional brake shoes of aircraft and automobile wheels.

Carbon/carbon frictional materials were prepared by the thermogradient gas-phase saturation of reinforcing carbon frames with a pyrolytic carbon matrix.

A range of tribological characteristics was estimated for sample carbon/carbon composites under full-scale simulation of the wheel brake operation. The samples were tested on the friction machine IM-58 type under conventional conditions of heat pulse friction (inertia moment of shaft is  $5.15 \text{ kg.cm.s}^2$ , rotation frequency is 6000 R/min, braking time is 22 s, running-in cycles 5 noms, classification cycles 15 noms, factor of mutual overlapping is 1).

Potential sample carbon/carbon composites have the following tribological characteristics: mean coefficient of friction is 0.35 to 0.39; wearing rate of rotational friction part is 0.75 microns/braking, wearing rate of fixed counterpart is 0.77 microns/braking, stability of friction coefficient is 0.8 at the bulk temperature of 600 to 650 °C and pressure of 0.4 to 0.5 MPa.

## MAGNETICAL SOFT HIGH-STRENGTH IRON FOR ACTIVE PARTS OF ELECTRIC MACHINES.

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Magnetoconductive parts of electric mashines and equipment usually made of Rolled electrotechnical steels. It is increase of production (manufacturing ) cost for the reason of high man-hours per job and small utilization coefficient of metal.

Main parameters of iron chemical contents, his structure, types of alloying and iron treatment with optimal composition of mechanical and magnetic properties and technological processes of casting production are determined. Results of testing of electric machines (asinhronyc electric motor) with heavy iron rotor and generetors with magnetocoductiving part of iron are shown.

Using of low alloying magnetically soft high strength for producing of magnetoconductive parts instead of parts of rolled steel allows to improve of staring properties capacity parameters of electric machines:

- increase of useful coefficient on 1.5 – 2%; capacity coefficient on 0.05

- 0.1; using of useful capacity on 9 – 11%, decrease of additional loss on 3 times , working temperature on 7-10°C.

Using of in induction rheostats allows to decrease copper loss on 30-40% and dimensions and at the same time increase of limits of electromagnetic parameters.



PERSPECTIVE USE OF THERMAL-GAS COATINGS FROM  
COMPOSITE MATERIALS IN THE AIRCRAFT TECHNICAL

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Wear and heat-corrosion resistant materials for the coatings were recovered to intend for reestablishment wearied out and strengthen of novel details by aircraft technical with an operating temperature up to 1200°C that operate in weak- and strongcorrosive environments and various loads.

Wear resistant materials have been developed at base on self-flux materials with addition other materials and refractory compounds with to receive amorphous-microcrystals structure of coatings.

Heat-corrosion materials have been developed at base Ni-Cr-Al-Y-Si with addition various elements and refractory compounds with to receive more highadhesion strength, heat-wear resistant of coatings.

These materials were recovered at details by detonation and supersonic plasma methods.

Supersonic plasma method has advantage before detonation method because that method using the cheap gas mixture "propane-buthane - air" or "methane - air". It has high productivity with special physical-chemical properties by himself coatings.

The early worked out materials were been to use in the aircraft technical:

- wear-resistant material of PKTCP type was sprayed on the main unit of flape of IL-76TD aircraft,
- heat- and wear-resistant materials of PNHA1 type was sprayed on flange unit of MI-2 helicopter GTE-350 compressor,
- heat- and corrosion-resistant material of PNHAITG type was sprayed on GTE first stage combustion chamber of YAK-38 aircraft

## **FIBER REINFORCED MATERIALS FOR HYBRID COMPOSITES**

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The fibrous materials, in particular, in the form of textile cloths, are widely applied in composites, however they have frequently simple structures comprising linear elements of one type, that considerably narrows opportunities of preparing composite materials with the given properties. At the same time mechanical technologies of fibrous materials used for manufacture of such materials, provide an opportunity of creation of rather complex connections of diverse elements, that allows to product reinforced materials with new integrate on properties.

The introduction of elements with various properties into fiber reinforced materials allows essentially to expand mechanical properties of composites. A choice and combination of such elements allow to have from hybrid engineering composites a necessary combination of properties (strength, crack resistance, erosion resistance etc.). But especially the use of hybrid textile materials in functional composites is important which in a number of cases can have a desired range of service properties only from diverse initial materials. A characteristic example of such materials are resistive, ones in which the necessary physical properties a obtained by creation.

In Institute for Materials Research, structures and technology of manufacturing many of woven and knitted single- and multilayer clothes, diverse textile thread, formed by a combination from natural and artificial fibres, and also wire of various materials and alloys which have allowed successfully to solve a number of tasks on designing of composites for various application, are developed. In particular, the appropriate materials are developed and on their basis are created devices of surface electroheating of industrial and household application that features high performance and low power consumption.

DEVELOPMENT AND PRODUCTION OF OXIDE AND CARBIDE  
DISPERSION STRENGTHENED COPPER OF THE DISCOM® TRADE  
MARK AT RUSSIAN ENTERPRISES

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Developed by Scientific and Technological Firm TECHMA Oxide and Carbide Dispersion Strengthened Copper (OCDS-Copper) of the DISCOM® trade mark representing Cu-Al-C-O, Cu-Ti-C-O, Cu-Cr-C-O, Cu-Al-Ti-C-O and other systems (Patents of the Russian Federation №№ 2113529, 2103135, 2118393, 2104139, 2103103, 2103134 and others; patent of Austria № 400580 and others) is produced according to the technology developed by this firm (patents of the Russian Federation №№ 2116370, 2117063) by both Scientific and Technological Firm TECHMA itself and Scientific and Production Enterprise KERMET and Scientific and Technological Centre KOMETA. OCDS-Copper production organizing is being finished in JSC URALLELECTROCOPPER.

The above mentioned material production is based on the technology of processing of initial powder mixture in attritors; cold compaction of granules got in attritors into briquettes; heating of the briquettes and their hot extrusion into bars, tubes and other semi-finished items, which, if necessary, can be subjected to finishing operations increasing their size accuracy and improving their surface quality.

Since all the technological process of OCDS-Copper semi-finished items production is carried out without any protectional and oxidizing-reducing media and it doesn't require any special complex equipment (besides attritors), then the semi-finished items cost doesn't surpass the best sorts of electrotechnical Bronze cost (CuCrZr, CuNiTiBe and others).

Taking into consideration that service-life of items made of OCDS-Copper is higher than service-life of similar items made of traditional sorts of Bronze, the OCDS-Copper customer finally gets considerably economical profit.

Long service-life ready-made items made of all the developed types of OCDS-Copper of the trade mark DISCOM® are produced and delivered to customers by Scientific and Technological Firm TECHMA.

# EFFECT OF MACRO- AND MICROSTRUCTURE OF TITANIUM IMPLANTS SURFACES ON THEIR ADHESION TO BONE TISSUE

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The paper presents results of investigations how a surface roughness, its physical-mechanical properties conditioned by the structure and the composition of the sprayed biocompatible or bioactive coatings, pore sizes and shape of source powder particles effect the adhesion of model cylindrical implants from powders of titanium of various grades. Investigations were made on laboratory animals. There are experimentally determined optimum parameters of micro- and macrostructures of the implant surface for ongrowth of bone tissue and for ingrowth in pores. It is shown that porous implants from spherical smooth titanium particles, cobalt-chromium-molybdenum alloy, gauzes etc. Do not ensure reliable cohesion with cells of bone tissue that results in nonstability of the implant and in decreasing the service life. It is provided that free of pores implants with the parameters of outer surface roughness  $R_a$  lower than  $3\text{ }\mu\text{m}$ , the thickness of biocompatible film  $\text{TiO}$ ,  $\text{TiO}_2$  being lower than  $1\text{ }\mu\text{m}$  or when bioactive  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  coating is absent have not practically adhesion to bone tissues. It is noted that deposition of hydroxyapatite on the inner pore surface additionally stipulates processes of osteointegration of the porous implant even of that which is made of sponge titanium powder particles.

The results of investigations of model implants are compared with literature data. There are additionally made investigations of a micro- and macrostructure of the surface which was reimplanted in clinics of hip joint endoprosthesis of European manufactures (Endo+, ALLOPRO Co., Switzerland, and SLPS system of various lots, ALTIMED Co., Byelarus). It is noted that even barely visible disturbances of technological modes result in considerable aggravation of adhesion to bone tissue of the composite implant with rough and porous areas of surface. There are made concrete recommendations as for improving constructive implant parameter.

### EXPERIENCE OF MANUFACTURING THIN-WALLED PROFILE RODS FROM COMPOSITE MATERIALS WITH AN INTEGRAL ASSEMBLY METHOD

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With the purpose of creation of extensible telescopic constructions the technology process of manufacturing of hybrid composite profile rods by a way of integral assembly was developed. For this purpose use previously curing elements (PCE) of a unbalanced structure, which gain the cylindrical shape after manufacturing at the expense of removal of internal stresses. The stabilization of the rod shape implements by curing together (PCE) on a cylindrical mandrel. The design of a rod represents a multilayer cylindrical envelope with one or several directing groove. Quantity and scheme reinforcement of a rod is determined by a thickness and stiffness. The additional strengthening of a rod can be realized by introduction between (PCE) indirectional or textile prepreg.

The developed technology process was realized at manufacturing hencasections construction intended for maintenance in conditions of outside space. The section represents thin-walled ( $h = 1$  mm) rod with one directing groove. Diameters of rods  $D = 100 \dots 200$  mm. The rods consist of two unbalanced structure (PCE) with an intermediate layer from prepreg of carbon fabric UT-900 impregnated epoxy resin. (PCE) were made from carbon prepreg fillet ELUR-0,08 impregnated epoxy resin. Outside rods are revetted by a fabric from kevlar threads, for maintenance high resistance to impact.

The technology process manufacturing of a rod included the following basic operations: forming by an elastic punch outside and internal (PCE) on the flat steel polished equipment having a longitudinal groove; the lining and fixing internal (PCE) on a cylindrical metal mandrel, having a longitudinal groove; the lining of layers fabric prepreg on internal (PCE); vacuum forming; the lining and fixing outside (PCE); a final curing together of a rod by a method of vacuum forming.

The realized technology process of integral assembly has allowed to receive the required characteristics of a rod with excellence surface and high accuracy of the sizes of a directing groove without consequent machining.

## SOL-GEL METHOD PREPARATION OF COLLOIDAL SILICA FOR FINAL POLISHING OF VARIOUS MATERIALS.

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Colloidal silica has been used for polishing since the early 1960's [1,2]. It was used initially to polish single crystal silicon for electronic applications and subsequently polycrystalline silicon for solar cells, gallium arsenide, indium phosphide, titanium, gadolinium gallium garnet and sapphire. At present colloidal silica is used for general metallographic final polishing of various materials [3].

A colloidal dispersion, referred to as a sol, contains very fine particles (1 to 100 nm in diameter) that remain in suspension for very long times. In colloidal silica, the particles are amorphous rather than crystalline and they have a negative electrical charge. Owing to electrostatic repulsion of particles from each other the stability of dispersion is increased. They are nearly insoluble in the dispersing medium.

Final polishing of semiconductor silicon wafers is made with the purpose of elimination of microdefects and infringed layer, formed after grinding. At present the final processing of wafers of semiconductor materials is made of water alkali suspension on the basis of expensive plasma powders  $\text{SiO}_2$  and ready suspensions "NALKO", "RODEL" and "SETON" (USA). With the purpose of their replacement industrial technology of reception of a colloidal silica on sol-gel method was developed and investigated.

### References

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# INVESTIGATION OF STRUCTURE AND PROPERTIES OF POROUS METALPOLYMER MATERIALS TO PURIFY LIQUIDS AND GASES FROM WATER DROPS AND FUMES

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To purify liquids and gases from hard particles as well as from water drops and fumes there are used porous materials subjected to water-repellency treatment or made of powders and fibers of hydrophobic materials i.e. bronze, polymers. Such materials segregate effectively only large water drops from a flow of fuel, motor oil or compressed air and do not arrest drops of size 0,1-0,2 mm and water fumes in a gaze flow the more so.

We developed 2 types of composite porous metalpolymer materials which are able to purify liquids and gazes from hard particles and drops with sizes up to 3-5  $\mu\text{m}$ , and gazes - from water fumes up to dew point - 10-13°C.

To purify fuel, motor and hydraulic oils bilayer porous materials are used. The base, 3-4mm in thickness, is made of sintered titanium powder of the ITX2-1 grade and is simultaneously characterized by good moisture absorption and small water yielding capacity. A hydrophobic layer, 1,0-2,0 mm in thickness, from the powder of fluoroplastic of the grade F4 is burned to the base. Filter elements from such materials were successfully tested in standard fuel filters of the «Ikarus» bus. Fineness of purification made 5  $\mu\text{m}$  and the effectiveness of water separation - 99,8-99,9%.

To purify and dry gazes there is used a three-layer porous material. In the direction of the flow of the contaminated and wet gas the layers are disposed as follows: fluoroplastic - titanium - bronze, there with a thickness of the titanium layer achieves 6-10 mm and that of a bronze one 2-3 mm. Pore sizes of the titanium and bronze layers are related to the pore size of fluoroplastic layer as 50-100/1 and 1,5-4,0/1 respectively such materials are used in moisture oil separators of WMO type with capacity 60-1200  $\text{m}^3/\text{hour}$ , fabricated in PMRI with PP.

WMO moisture - oil separators are used on tens of enterprises of the Republic of Belarus and of the Russian federation.

# **INFLUENCE OF CHARACTERISTICS OF STRUCTURES POROUS FORMED FROM METALS FIBROUS IN PROCESS OF INITIAL BOILING FOR HEAT TRANSFER LIQUIDS**

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The presence of porous structures on heat transfer surfaces for equipment functioning in boiling regimes, for example, in thermosiphons and heat pipes, result in change of density values of heat flows and the parameters of initial liquids boiling. The change effected is conditioned by the influence of porous structures on the boundary layers of liquid.

The potential presence of bubbles centers of steam and the favorable conditions for their activity improves the initial boiling process.

The data findings of researches on initial boiling on porous surfaces are few and contradictory. Complex researches on the influence of characteristics of different porous structures on density of heat flow and the difference of temperature is limited.

Influence of porous structures formed from fibrous metals on the initial boiling of water in conditions of the free movement of liquid and in conditions of transport capillary of liquid is investigated.

The data findings permitted receive the appraisal for influence of parameters of porous structures on the initial boiling. The data findings received in wide diapasons of change of structurals and thermophysicals characteristics of porous structures formed from fibrous metals (the thickness  $\delta$ , the porosity  $\Theta$ , and the heat conductivity  $\lambda$ ).

The porosity  $\Theta$ , the middle diameter of pores  $D$  and the heat conductivity  $\lambda$  of porous structures affected on the values of difference of temperatures of initial boiling. The data findings ( $\Delta T = f(\delta, \Theta, D, \lambda)$ ) received and compared for conditions of capillary transport of water. The formulae for calculations of difference of temperature for the initial boiling of water on the porous surfaces formed from fibrous metals were obtained.



## Natural (in-situ) composites

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The composites represent a very important group of advanced materials. As a rule, such materials are produced artificially. In this case the reinforcing phase (plates, fibres etc.) is added into the metallic, ceramic or polymer matrix by using different technologies. It is possible to obtain the unusual combination of physical and mechanical properties by changing phase type, form and volume content.

The natural (in situ) composites are the very interesting representatives of such materials. The reinforcement of these composites is effected with the second phase formed in eutectic crystallisation. The production of such in situ composites can be accompanied with directed crystallisation of eutectics. The basis for designing the eutectic composites is the investigation of the phase equilibrium in the double, triple and multicomponent systems. The task of this investigation is the determination of suitable eutectic compositions.

The examples of the eutectic composites on basis of ceramic, metallic or intermetallic matrix have been considered. The comparison of Ti-based SiC reinforced MMC and in situ composites is given.

It has been shown that SiC MMC (Ti-based) composites with the longitudinal fibre orientation possess the highest properties. However, these composites are characterised with the high anisotropy of mechanical properties. Besides, their cost is extremely high (from 2000 to 11000 USD per kg). The cost of eutectically reinforced Ti-Si-Al-Zr materials is at the same level as that of the conventional Ti-alloys. It should be also mentioned that they do not possess any anisotropy of mechanical properties. The detail from these alloys can be produced by conventional technologies: casting, mould casting, forging, rolling, extrusion etc.

The examples of eutectic compositions based on refractory metals are given. The problem of obtaining the maximum heat resistance is discussed.

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